TITLE OF THE INVENTION: PROTECTIVE FILM COMPOSITION, MANUFACTURING METHOD OF SEMICONDUCTOR DEVICE, AND LASER CUTTING METHOD

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The invention relates to a protective film composition, a manufacturing method of a semiconductor device, and a laser cutting method, and more particularly relates to a protective film composition used for laser cutting of semiconductor wafers, etc., a manufacturing method of a semiconductor device processed by laser cutting, and a laser cutting method.

Description of Related Art

[0002] In the manufacturing process of a semiconductor device, each semiconductor chip is obtained by dicing and separating a semiconductor wafer on which various devices are laminated.

As the cutting method, laser cutting has always been used in recent years.

The so-called laser cutting is a method of irradiating an object with a laser to cut the object into a desired shape, wherein machining may be performed with high accuracy in a short time.

In laser cutting, after the substrate is irradiated with a laser, there are cases where the substrate absorbs the laser so that the substrate is melted due to the thermal energy thereof, and the hot melt (debris) is adhered to the surface of the device. If the

debris is adhered to the surface of the device, the quality of the semiconductor chip is decreased.

As a processing method to protect the surface of the device from debris, a processing method in which a protective film is formed on the surface of a substrate and laser light is irradiated through the protective film has been proposed. As the protective film, a water-soluble protective film that may be cleaned and removed after laser cutting has been studied.

[0003] Specifically, Taiwan Published Patent No. 201614017 discloses a protective film composition for laser cutting, which contains a water-soluble resin, a resin capsule containing a laser light absorbing agent, and a water-based solvent.

[0004] However, the protective film composition described above has worse leveling property, and therefore may not be accepted by the industry.

SUMMARY OF THE INVENTION

[0005] In view of the issue above, the invention provides a protective film composition that may alleviate the issue of worse leveling property.

[0006] The invention provides a protective film composition including: a water-soluble resin (A), a laser light absorbing agent (B), and a solvent (C), wherein the water-soluble resin (A) includes a polyvinylpyrrolidone-based water-soluble resin (A-1), and a K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 75 to 150.

[0007] In an embodiment of the invention, the water-soluble resin (A) further includes a polyvinylpyrrolidone-based water-soluble resin (A-2), and a K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 5 to 70.

[0008] In an embodiment of the invention, the K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 80 to 140.

[0009] In an embodiment of the invention, the K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 80 to 130.

[0010] In an embodiment of the invention, the K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 10 to 65.

[0011] In an embodiment of the invention, the K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 15 to 65.

[0012] In an embodiment of the invention, based on 100 parts by weight of the water-soluble resin (A), a usage amount of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 25 parts by weight to 65 parts by weight, and a usage amount of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 35 parts by weight to 75 parts by weight.

[0013] In an embodiment of the invention, based on 100 parts by weight of the water-soluble resin (A), a usage amount of the laser light absorbing agent (B) is 1 part by weight to 30 parts by weight, and a usage amount of the solvent (C) is 500 parts by weight to 3000 parts by weight.

[0014] In an embodiment of the invention, the protective film composition is used for a laser cutting application.

[0015] The invention further provides a manufacturing method of a semiconductor device, including:

a step of applying the protective film composition above on a substrate to form a protective layer,

a step of irradiating the substrate with a laser light through the protective layer to perform laser cutting, and

a step of washing the substrate with water after laser cutting and removing the protective layer from the substrate.

[0016] The invention also provides a laser cutting method, including:

a step of applying the protective film composition above on a substrate to form a protective layer,

a step of irradiating the substrate with a laser light through the protective layer to perform laser cutting, and

a step of washing the substrate with water after laser cutting and removing the protective layer from the substrate.

[0017] Based on the above, the protective film composition of the invention contains the polyvinylpyrrolidone-based water-soluble resin (A-1) with a specific K value range and the laser light absorbing agent (B), and therefore the technical issue of worse leveling property in the prior art may be alleviated.

[0018] In addition, the protective film composition according to the invention contains a water-soluble laser light absorbing agent in addition to the water-soluble resin. Therefore, the protective film formed on the wafer surface by coating and drying the protective film composition exhibits a high degree of absorption of laser light, so when irradiated with laser light, the protective film may be thermally decomposed in time along a street line and be processed by laser. Therefore, the protective film may be effectively protected from peeling due to vapor pressure and the like of the thermal decomposition product of the substrate formed by exposure to laser light. In addition,

a water-soluble dye and the like used as the water-soluble laser light absorbing agent has high affinity for the wafer surface. Therefore, the adhesion of the protective film is improved, and the protective film, especially near the street line, may be effectively prevented from peeling off the wafer surface. Accordingly, the protective film is formed by the protective film composition of the invention, and laser cutting is performed by laser light, thereby effectively preventing debris from being deposited all over the surface of the diced chip.

[0019] In addition, as a general laser light, a laser light with a wavelength of 355 nm is used. When cutting with such laser light, by adjusting the amount of laser light absorbing agent used, the g absorption coefficient k of the protective film (solid of the protective film composition) is within the range of 3×10^{-3} abs • L/g to 2.5×10^{-1} abs • L/g (abs: degree of absorption). In this way, a uniform processing result may be achieved along the street line of fine width.

[0020] In order to make the aforementioned features and advantages of the invention more comprehensible, embodiments are described in detail below.

DESCRIPTION OF THE EMBODIMENTS

[0021] <Protective film composition>

The invention provides a protective film composition including a water-soluble resin (A), a laser light absorbing agent (B), and a solvent (C), and optionally includes an additive (D). The water-soluble resin (A) includes a polyvinylpyrrolidone-based water-soluble resin (A-1), and optionally includes a polyvinylpyrrolidone-based water-soluble resin (A-2) and other water-soluble resins

(A-3). The components of the protective film composition used in the invention are described in detail below.

Water-soluble resin (A)

[0022] The water-soluble resin (A) includes the polyvinylpyrrolidone-based water-soluble resin (A-1) with a K value of 75 to 150. However, from the viewpoint of improving leveling property, it is better to use the polyvinylpyrrolidone-based water-soluble resin (A-2) with a K value of 5 to 70 in combination, and the other water-soluble resins (A-3) may be added as appropriate.

Polyvinylpyrrolidone-based water-soluble resin (A-1)

[0023] The K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) ranges from 75 to 150, preferably from 80 to 140, and more preferably from 80 to 130.

[0024] The K value of the water-soluble resin is a value indicating the size of the molecular weight by the Fikentscher method, and may be obtained by the following measurement method as shown in the following formula (1). When the K value is less than 20, the viscosity of a 5% (g/100 mL) solution is measured, and when the K value is 20 or more, the viscosity of a 1% (g/100 mL) solution is measured. The concentration of the sample is calculated from dry matter. When the K value is 20 or more, 1.0 g of the sample is accurately measured and placed into a 100 mL measuring flask, then distilled water is added at room temperature, vibrated, and at the same time, completely dissolved, and then distilled water is added to make the solution exactly 100 mL. After the sample solution is placed in a thermostat (25±0.2 °C) for 30 minutes, measurement

is performed using an Uberoude-type viscometer. The sample solution is measured for the time it takes to flow between two mark lines. The measurement is performed several times to obtain an average value. In order to determine relative viscosity, the distilled water is also measured in the same way. According to Hagenbach-Couette correction value, two obtained flow times are corrected.

[0025]

$$\text{K value} = \frac{\sqrt{300C \log Z + (C + 1.5C \log Z)^2} + 1.5C \log Z - C}{0.15C + 0.003C^2} \quad (1)$$

In formula (1), Z is the relative viscosity of the solution with concentration C (η_{rel})

C is the concentration of the sample (%: g/100 mL)

The relative viscosity η_{rel} is obtained by the following formula (2).

η_{rel}=(flow time of solution)÷(flow time of water) (2)

[0026] Specific examples of the polyvinylpyrrolidone-based water-soluble resin (A-1) may include the following commercially available products: PITZCOL K-90 (K value=88 to 100, made by Dai-Ichi Kogyo Seiyaku Co., Ltd.), PVP K-85 (K value=83 to 88, made by Nippon Shokubai Co., Ltd.), PVP K-120 (K value=114 to 130, made by Nippon Shokubai Co., Ltd.) The polyvinylpyrrolidone-based water-soluble resin (A-1) may be used alone or in combination of two or more.

[0027] Based on a usage amount of 100 parts by weight of the water-soluble resin (A), the usage amount of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 25 parts by weight to 65 parts by weight, preferably 30 parts by weight to 65 parts by

weight, and more preferably 30 parts by weight to 60 parts by weight. When the polyvinylpyrrolidone-based water-soluble resin (A-1) is not included in the water-soluble resin (A), the leveling property of the protective film composition is poor.

Polyvinylpyrrolidone-based water-soluble resin (A-2)

[0028] The K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) ranges from 5 to 70, preferably from 10 to 65, and more preferably from 15 to 65.

[0029] Specific examples of the polyvinylpyrrolidone-based water-soluble resin (A-2) may include the following commercially available products: PITZCOL K-30 (K value=26 to 35, made by Dai-Ichi Kogyo Seiyaku Co., Ltd.), PVP K-12 (K value=10 to 14, made by Nippon Shokubai Co., Ltd.), PVP K-15 (K value=13 to 19, made by Nippon Shokubai Co., Ltd.), PVP K-60 (K value=50 to 62, made by Nippon Shokubai Co., Ltd.) The polyvinylpyrrolidone-based water-soluble resin (A-2) may be used alone or in combination of two or more.

[0030] Based on a usage amount of 100 parts by weight of the water-soluble resin (A), the usage amount of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 35 parts by weight to 75 parts by weight, preferably 35 parts by weight to 70 parts by weight, and more preferably 40 parts by weight to 70 parts by weight. When the water-soluble resin (A) further includes the polyvinylpyrrolidone-based water-soluble resin (A-2), the leveling property of the protective film composition may be further improved.

Other alkali-soluble resins (A-3)

[0031] In addition to the polyvinylpyrrolidone-based water-soluble resin (A-1) and the polyvinylpyrrolidone-based water-soluble resin (A-2), under the premise of not affecting

the effect of the invention, the water-soluble resin (A) may further include the other water-soluble resins (A-3).

[0032] The other water-soluble resins (A-3) are used as the base of the protective film, and are not limited as long as they are a material that may form a film by coating and drying in a solvent such as water. Examples thereof include polyvinyl alcohol, polyethylene glycol with 5 or more ethyleneoxy repeating units, polyoxyethylene, methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, polyacrylic acid, polyvinyl alcohol-polyacrylic acid block copolymer, polyvinyl alcohol-polyacrylate block copolymer, and polyglycerol. The other water-soluble resins (A-3) may be used alone or in combination of two or more.

[0033] The protective film formed on the wafer surface in the invention is removed by washing with water after laser processing. As for the other water-soluble resins (A-3), if the washability of the protective film is taken into consideration, it is preferable to use a resin having only an ether linkage or a hydroxyl group as the polar group, such as polyvinyl alcohol or polyethylene glycol. This is because a water-soluble resin with a polar group such as a carboxyl group or a tertiary amine is tightly bonded to the wafer surface (chip surface), and may remain on the wafer surface after washing with water. Moreover, the adhesion of a resin having only an ether chain or a hydroxyl group is relatively weaker, so the resin may be effectively prevented from remaining after washing with water. From the viewpoint of washability, the polymerization degree or molecular weight of the other water-soluble resins (A-3) is preferably lower. Taking polyvinyl alcohol as an example, the degree of polymerization thereof is preferably about 300. However, a water-soluble resin with a high degree of polymerization or

high molecular weight has low water-washability, but here, when used in combination with the following plasticizer, the reduction in water-washability is prevented.

[0034] Based on a usage amount of 100 parts by weight of the water-soluble resin (A), the usage amount of the other water-soluble resins (A-3) is 0 parts by weight to 80 parts by weight, preferably 0 parts by weight to 50 parts by weight, and more preferably 0 parts by weight to 30 parts by weight.

Laser light absorbing agent (B)

[0035] The laser light absorbing agent (B) may adopt a water-soluble dye, a water-soluble pigment, and a water-soluble ultraviolet light absorbing agent. These absorbing agents are all water-soluble and may advantageously be uniformly present in the protective film. In addition, they exhibit good affinity to the wafer surface and may form a protective film that is highly bonded to the wafer surface. In addition, their advantage is that the solutions thereof have high storage stability, and there are no disadvantages such as phase separation or sedimentation during storage, and satisfactory coating property may be ensured. If a water-insoluble laser light absorbing agent such as a pigment is used, the laser absorption power of the protective film is changed, or the storage stability or coating property is poor, so that a protective film with uniform thickness is difficult to be formed.

[0036] The water-soluble dye may be selected from, for example: an azo dye (monoazo and polyazo dyes, a metal complex salt azo dye, a pyrazolinone azo dye, a stilbene dye, a thiazole azo dye), an anthraquinone dye (an anthraquinone derivative, an anthrone derivative), an indigo dye (an indigo derivative, a thioindigo derivative), a

phenolcyanine dye, a carbocation dye (a diphenylmethane dye, a triphenylmethane dye, a dibenzopyran dye, an acridine dye), a quinone imine dye (an azine dye, an oxazine dye, a thiazide dye), a methine dye (a cyan dye, an azomethine dye), a quinoline dye, a nitroso dye, a benzoquinone dye and a naphthoquinone dye, a naphthalimide dye, a perinone dye, and other dyes.

[0037] As the water-soluble pigment, from the viewpoint of environmental burden, etc., a food additive pigment is preferred, such as: Edible Red No. 2, Edible Red No. 40, Edible Red No. 102, Edible Red No. 104, Edible Red No. 105, Edible Red No. 106, Edible Yellow NY, Edible Yellow No. 4 Lemon Yellow, Edible Yellow No. 5, Edible Yellow No. 5 Sunset Yellow FCF, Edible Orange AM, Edible Vermilion No. 1, Edible Vermilion No. 4, Edible Vermilion No. 101, Edible Blue No. 1, Edible Blue No. 2, Edible Green No. 3, Edible Melon Color B, and Edible Egg Color No. 3.

[0038] Examples of the water-soluble ultraviolet light absorbing agent may include: 4,4'-dicarboxybenzophenone, benzophenone-4-carboxylic acid, 2-carboxynaphthoquinone, 1,2-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, and 2,7-naphthalenedicarboxylic acid and sodium salt, potassium salt, ammonium salt, and quaternary ammonium salt thereof, 2,6-anthraquinone disulfonic acid sodium salt, 2,7-anthraquinone disulfonic acid sodium salt, and ferulic acid, wherein ferulic acid is preferred.

[0039] The amount of the laser light absorbing agent (B) is the amount that may ensure the desired laser light absorption. For example, if a laser light with a wavelength of 355 nm is used for processing, the amount of the laser light absorbing

agent (B) is such that the g absorption coefficient k of the protective film (that is, the solid of the protective film composition) is preferably within the range of 3×10^{-3} abs • L/g to 2.5×10^{-1} abs • L/g (abs: absorption). If the g absorption coefficient k is lower than the above range, the laser light absorption of the protective film is so low that the thermal decomposition of the protective film due to laser light irradiation is much lower than that of a silicon substrate. As a result, there is a tendency for the film to peel off due to the vapor pressure of the thermal decomposition product, and debris is formed at the peripheral edge portion of the chip. If the g absorption coefficient k is higher than the above range, when laser light is irradiated, thermal decomposition of the protective film may easily occur due to, for example, reflection from the substrate. Therefore, the processing width of the laser is larger than the laser spot diameter, so the laser is not suitable in particular for cutting along a street line with fine linewidth.

[0040] In addition, if the laser light absorbing agent (B) with a maximum absorption wavelength range in the range of the laser light wavelength is selected, a small amount of use may ensure that the g absorption coefficient k is within the above range. If a laser light absorbing agent that may not meet this condition is selected, a large amount is needed to ensure that the g absorption coefficient k is within the above range. However, if the amount of the laser light absorbing agent (B) is too large, when the protective film composition containing the laser light absorbing agent (B) is coated and dried to form a protective film, phase separation may occur between the laser light absorbing agent (B) and the water-soluble resin (A). If the amount of the laser light absorbing agent (B) is too small, the distribution of the laser light absorbing agent (B) in the protective film may be uneven.

[0041] Based on a usage amount of 100 parts by weight of the water-soluble resin (A), the usage amount of the laser light absorbing agent (B) is 1 part by weight to 30 parts by weight, preferably 3 parts by weight to 30 parts by weight, and more preferably 5 parts by weight to 25 parts by weight.

Solvent (C)

[0042] The solvent (C) is not particularly limited as long as it may dissolve the water-soluble resin (A) and the laser light absorbing agent (B). Examples of the solvent (C) may include water, alcohol, ester, alkylene glycol, alkylene glycol monoalkyl ether, and alkylene glycol monoalkyl ether acetate. In particular, water and alkylene glycol monoalkyl ether are preferred. As the alkylene glycol monoalkyl ether, propylene glycol monomethyl ether (PGME) is preferred. For the working environment, the best solvent is water or a mixed solvent containing water.

[0043] Based on a usage amount of 100 parts by weight of the water-soluble resin (A), the usage amount of the solvent (C) is 500 parts by weight to 3000 parts by weight, preferably 800 parts by weight to 3000 parts by weight, and more preferably 1000 parts by weight to 2500 parts by weight.

Additive (D)

[0044] In the invention, in addition to the water-soluble resin (A) and the laser light absorbing agent (B), an additive (D) may be added to the protective film composition without affecting the effect of the invention. Specific examples thereof include a plasticizer and a surfactant.

[0045] A plasticizer is used to improve the washability of the protective film after laser processing. Especially when the water-soluble resin (A) with high molecular weight is used, a plasticizer is preferred. Another advantage of using a plasticizer is that it may suppress the carbonization of the water-soluble resin caused by laser light irradiation. The plasticizer is preferably a water-soluble, low-molecular-weight compound. Examples thereof are ethylene glycol, triethylene glycol, tetraethylene glycol, ethanolamine, and glycerin. The compounds may be used alone or in combination of two or more. The amount of the plasticizer is such that phase separation does not occur between the plasticizer and the water-soluble resin (A) after the protective film composition is coated and dried. For example, based on a usage amount of 100 parts by weight of the water-soluble resin (A), the recommended amount thereof is 75 parts by weight or less, preferably 20 parts by weight to 75 parts by weight.

[0046] A surfactant is used to improve coating property and further improve the storage stability of the protective film composition. Any surfactant of nonionic, cationic, anionic, or amphoteric type may be used as long as it is water-soluble.

[0047] Examples of the nonionic surfactant include nonylphenol, higher alcohol-based, polyhydric alcohol-based, polyoxyethylene glycol-based, polyoxyethylene alkyl ester-based, polyoxyethylene alkyl ether-based, polyoxyethylene alkylphenol ether-based, and polyoxyethylene sorbitan alkyl ester-based surfactants. Examples of the cationic surfactant are quaternary ammonium salt and amine salt. Examples of the anionic surfactant are alkylbenzene sulfonic acid and a salt thereof, alkyl sulfate, methyl taurate, and ether sulfonate. Examples of the amphoteric surfactant include imidazoline betaine-based, amidopropyl betaine-based, and amino

dipropionate-based surfactants. The surfactant may be used alone or in combination of two or more. The amount of the surfactant may be tens of ppm or hundreds of ppm based on the protective film composition.

[0048] In the protective film composition for laser cutting of the invention, the solid component content of the protective film composition needs to be set according to the type, degree of polymerization, or molecular weight of the water-soluble resin used, so that the protective film composition has appropriate coating property. If the solid component content is too high, coating is difficult, thus easily causing uneven thickness or ingress of bubbles. If the solid component content is too low, when the protective film composition is coated on a wafer surface, it may drip, and the film thickness (protective film thickness) is difficult to be adjusted after drying. Therefore, although the solid component content in the protective film composition varies depending on the water-soluble resin (A) used, etc., it is preferably set to about 3 wt% to 30 wt%. The amount of the water-soluble resin (A) in the solid component is usually 5 wt% or more. This is preferable from the viewpoint of providing adequate strength of the protective film and preventing debris from being deposited on the chip surface.

<Manufacturing method of protective film composition>

[0049] The manufacturing method of the protective film composition of the invention is not particularly limited, and each of the components may be mixed for the preparation. The mixing of each component is usually performed in the range of 0 °C to 100 °C. Moreover, after each component is mixed, filtration is preferably performed by a filter, for example. Filtration may be performed in multiple stages or repeated

multiple times. In addition, the filtered protective film composition may be refiltered.

[0050] The filter may be used without particular limitation as long as it has been used in a filtration application and the like. Examples may include: filters of, for example, a fluororesin such as polytetrafluoroethylene (PTFE), a polyamide-based resin such as nylon-6, nylon-6,6, and a polyolefin resin (including high-density, ultra-high molecular weight) such as polyethylene and polypropylene (PP). Among the raw materials, polypropylene (including high-density polypropylene) and nylon are preferred.

[0051] The pore size of the filter is preferably about 0.5 μm to 100 μm, for example. By setting the pore diameter in the above range, clogging of filtration may be suppressed, and fine foreign substances such as impurities and aggregates contained in the composition may be reliably removed.

[0052] When a filter is used, different filters may be combined. At this time, the filtration in the first filter may be performed only once, or may be performed two or more times. When different filters are combined to perform two or more filtrations, the pore size after the second filtration is preferably the same or smaller than the pore size of the first filtration. In addition, first filters with different pore sizes may also be combined within the above range. The pore size here is as provided in the nominal value of the filter manufacturer. A commercially available filter may be selected from various filters provided by, for example, NIHON PALL Co., Ltd., Advantec Toyo Co., Ltd., Nihon Entegris Co., Ltd. (formerly Nihon Mykrolis Co., Ltd.), or KITZ MICRO FILTER Co., Ltd.

<Manufacturing method of semiconductor device and laser cutting method>

[0053] Next, the manufacturing method and laser cutting method of the semiconductor device of the invention are described.

[0054] The manufacturing method of the semiconductor device and the laser cutting method of the invention include: a step of applying the protective film composition of the invention on a substrate to form a protective layer (step 1);

a step of irradiating the substrate with a laser light through the protective layer to perform laser cutting (step 2);

a step of washing the substrate with water after laser cutting and removing the protective layer from the substrate (step 3).

[0055] Regarding the laser cutting method of the invention, examples used in the manufacture of semiconductor devices may be cited, which are described below. However, the laser cutting method of the invention may also be applied to cutting substrates in addition to the manufacture of semiconductor devices.

In the following, each step of the manufacturing method and laser cutting method of the semiconductor device of the invention is described.

[0056] <<Step 1>>

In step 1, the protective film composition of the invention is applied on a substrate to form a protective layer.

Any substrate known in semiconductor devices may be used without limitation, for example, and examples thereof may include a silicon substrate and a compound semiconductor substrate, for example. Specific examples of the compound semiconductor substrate may include a SiC substrate, a SiGe substrate, a ZnS substrate, a ZnSe substrate, a GaAs substrate, an InP substrate, a GaN substrate, and the like.

[0057] A mechanical structure or circuit may be formed on the surface of the substrate. Examples of the substrate on which a mechanical structure or a circuit is formed may include: a micro electro mechanical system (MEMS), a power device, an image sensor, a micro sensor, a light-emitting diode (LED), an optical device, an interposer, an embedded device, a micro device, etc.

[0058] The thickness of the substrate is preferably 10 μm or more, more preferably 20 μm or more, and particularly preferably 50 μm or more. The upper limit is, for example, preferably 500 μm or less, more preferably 200 μm or less, and particularly preferably 100 μm or less. In the invention, a good cutting shape may be formed in laser cutting even for a substrate of a brittle material containing, for example, a low dielectric constant material.

[0059] Examples of the application method of the protective film composition may include: a casting method, a knife coating method, a wire bar coating method, a spray coating method, a dip coating method, a droplet coating method, an air knife coating method, a curtain coating method, an inkjet method, a spin coating method, a Langmuir-Blodgett (LB) method, etc. In the invention, a casting method, a spin coating method, and an inkjet method are particularly preferred.

[0060] The thickness of the protective film is not particularly limited. The thickness may be adjusted appropriately according to objective and application. For example, the thickness is preferably 0.5 μm to 20 μm, more preferably 1 μm to 5 μm.

[0061] <<Step 2>>

Then, the substrate is irradiated with laser light through the protective layer, and the laser light is scanned along the line of the substrate to be cut and processed to

perform laser cutting.

Since the protective film contains a laser light absorbing agent, it has high laser light absorption energy. If the laser light is irradiated to the substrate through the protective film, the expansion of the laser light in the film may be suppressed. In addition, at the location where the laser light is irradiated, at the same time as the thermal decomposition of the substrate or before the thermal decomposition of the substrate, the protective film is thermally decomposed and fractured.

[0062] In addition, in the portion where the laser light is not irradiated, the substrate is covered with the protective film, so that the surface of the substrate may be protected from debris such as thermal decomposition products of the substrate, and the adhesion of debris may be prevented, for example.

[0063] In addition, the protective film is less likely to cause degradation of the performance of the laser light absorbing agent due to laser irradiation, and may efficiently suppress the expansion of the laser light in the protective film. Therefore, when laser cutting is performed on a thick substrate, the protective film may also effectively suppress the expansion of the laser light, and as a result, a good cutting shape may be formed.

[0064] The laser light source used for laser cutting is not particularly limited. Examples include: yttrium aluminum garnet (YAG) laser, yttrium lithium fluoride (YLF) laser, yttrium vanadate (YVO4) laser, excimer laser, semiconductor laser, etc.

[0065] The wavelength of the laser light is preferably 200 nm to 600 nm, more preferably 300 nm to 500 nm. The spot diameter of the laser light is not particularly limited and is preferably 0.1 μm to 50 μm, and more preferably 1 μm to 20 μm, for

example.

[0066] Furthermore, the spot diameter (D) of the laser light may be calculated according to the following formula (3) when the pulsed laser light is condensed and irradiated by the objective lens of the condenser.

$$D=4\times\lambda\times f/(\pi\times W) \qquad (3)$$

In formula (3), D is the spot diameter of the laser light (μm)

λ is the wavelength of pulsed laser light (μm)

W is the diameter of the pulsed laser light incident on the condenser objective lens (mm)

f is the focal length of the condenser objective lens (mm)

[0067] <<Step 3>>

Next, the substrate is washed with water after laser cutting and the protective layer is removed from the substrate.

Since the protective film contains a water-soluble resin, it may be easily removed from the substrate by washing with water. In addition, with the removal of the protective film, debris etc. adhered to the protective film is also washed away.

[0068] The water washing conditions of the protective film are not particularly limited. The conditions may be adjusted appropriately according to the thickness and the like of the protective film.

In this way, a semiconductor device such as a separated semiconductor chip may be obtained.

<Examples>

[0069] The following examples are used to further describe the invention. However, it should be understood that, the examples are only exemplary, and are not intended to limit the implementation of the invention.

[0070] Example 1 to Example 13 and Comparative example 1 to Comparative example 6 of the protective film composition are described below:

[0071] Example 1

100 parts by weight of PVP K-85 (equivalent to the polyvinylpyrrolidone water-soluble resin (A-1), referred to as A-1-1) and 10 parts by weight of Edible Red No. 102 (equivalent to the laser light absorbing agent (B), referred to as B-1) were added to a mixed solvent of 100 parts by weight of propylene glycol monomethyl ether (C-1) and 400 parts by weight of water (C-2), then, at room temperature, the mixture was added to a mixer equipped with a stirrer and stirred at 500 rpm for 1 hour to obtain the protective film composition of Example 1.

[0072] Example 2 to Example 13

The protective film compositions of Example 2 to Example 13 were prepared by the same steps as Example 1, and the difference is that the component types and the usage amounts of the water-soluble resin (A), the laser light absorbing agent (B), and the solvent (C) were changed (as shown in Tables 1 and 2).

[0073] Comparative example1 to Comparative example 6

The protective film compositions of Comparative example 1 to Comparative example 6 were prepared by the same steps as Example 1, and the difference is that the

component types and the usage amounts of the water-soluble resin (A), the laser light absorbing agent (B), and the solvent (C) were changed (as shown in Table 2).

[0074] The compounds corresponding to the labels in Table 1 and Table 2 are as shown below:

Abbreviation	Component
A-1-1	PVP K-85 (K value=83 to 88, made by Nippon Shokubai Co., Ltd.)
A-1-2	PITZCOL K-90 (K value=88 to 100, made by Dai-Ichi Kogyo Seiyaku Co., Ltd.)
A-1-3	PVP K-120 (K value=114 to 130, made by Nippon Shokubai Co., Ltd.)
A-2-1	PVP K-12 (K value=10 to 14, made by Nippon Shokubai Co., Ltd.)
A-2-2	PVP K-15 (K value=13 to 19, made by Nippon Shokubai Co., Ltd.)
A-2-3	PITZCOL K-30 (K value=26 to 35, made by Dai-Ichi Kogyo Seiyaku Co., Ltd.)
A-2-4	PVP K-60 (K value=50 to 62, made by Nippon Shokubai Co., Ltd.)
A-3-1	Polyvinyl alcohol PXP-05 (manufactured by Japan Vam & Poval Co., Ltd.)
A-3-2	Polyvinyl alcohol PXP-18 (manufactured by Japan Vam & Poval Co., Ltd.)
B-1	Edible Red No. 102
B-2	2,6-naphthalenedicarboxylic acid
B-3	Anthraquinone-2,6-disulfonic acid disodium salt
B-4	Ferulic acid
C-1	Propylene glycol methyl ether (PGME)
C-2	Water

[0075] [Table 1]

Component (parts by weight)		Example									
		1	2	3	4	5	6	7	8	9	10
Polyvinylpyrrolidone-based water-soluble resin (A-1)	A-1-1	100	-	-	50	25	-	-	35	-	-
	A-1-2	-	100	-	50	-	40	-	-	45	-
	A-1-3	-	-	100	-	-	-	65	-	-	60
Polyvinylpyrrolidone-based water-soluble resin (A-2)	A-2-1	-	-	-	-	-	-	-	65	-	-
	A-2-2	-	-	-	-	-	-	-	-	55	-
	A-2-3	-	-	-	-	-	-	-	-	-	30
	A-2-4	-	-	-	-	-	-	-	-	-	-
Other alkali-soluble resins (A-3)	A-3-1	-	-	-	-	75	60	-	-	-	-
	A-3-2	-	-	-	-	-	-	35	-	-	-
Laser light absorbing agent (B)	B-1	10	-	-	-	1	-	-	-	25	-
	B-2	-	3	-	-	-	15	-	-	-	8
	B-3	-	-	5	-	-	-	28	-	-	-
	B-4	-	-	-	20	-	-	-	10	-	-
Solvent (C)	C-1	100	150	350	100	100	150	350	100	150	350
	C-2	400	750	1650	400	400	750	1650	400	750	1650
Leveling property evaluation		○	○	○	○	○	○	○	◎	◎	◎

[0076] [Table 2]

Component (parts by weight)		Example			Comparative example					
		11	12	13	1	2	3	4	5	6
Polyvinylpyrrolidone-based water-soluble resin (A-1)	A-1-1	-	30	-	-	-	-	-	-	-
	A-1-2	50	-	25	-	-	-	-	-	-
	A-1-3	-	-	30	-	-	-	-	-	-
Polyvinylpyrrolidone-based water-soluble resin (A-2)	A-2-1	-	35	45	100	-	-	100	-	-
	A-2-2	-	-	-	-	50	-	-	50	-
	A-2-3	-	35	-	-	-	-	-	-	-
	A-2-4	50	-	-	-	-	-	-	-	-
Other alkali-soluble resins (A-3)	A-3-1	-	-	-	-	-	100	-	-	100
	A-3-2	-	-	-	-	50	-	-	50	-
Laser light absorbing agent (B)	B-1	10	-	-	-	-	-	5	-	-
	B-2	-	-	30	-	-	-	-	10	-
	B-3	20	-	-	-	-	-	-	-	20
	B-4	-	15	-	-	-	-	-	-	-
Solvent (C)	C-1	500	500	500	150	200	300	150	200	300
	C-2	2500	2000	2000	750	800	1200	750	800	1200
Leveling property evaluation		◎	◎	◎	X	X	X	X	X	X

<Evaluation methods>

[0077] Leveling property

100 mL of the protective film composition of the Examples and the Comparative examples were taken respectively and placed into a 500 mL beaker, and then after the protective film compositions were stirred continuously at 500 rpm for 4 hours, the surface tension of the protective film compositions was measured using a surface tension meter (CBVP-2, Kyowa).

The leveling property criteria for the evaluation of surface tension are as follows:

◎: surface tension<35 mN/m

○: 35 mN/m≦surface tension<40 mN/m

△: 40 mN/m≦surface tension<50 mN/m

╳: 50 mN/m≦surface tension

[0078] It may be seen from Table 1 and Table 2 that the protective film compositions of the invention (Examples 1 to 13) adopt the polyvinylpyrrolidone-based water-soluble resin (A-1) with a K value of 75 to 150 and the laser light absorbing agent (B), and therefore the leveling property evaluation thereof is good.

[0079] In contrast, when the polyvinylpyrrolidone-based water-soluble resin (A-1) with a K value of 75 to 150 is not used in the protective film compositions (Comparative examples 1 to 6), the resulting protective film compositions have the issue of worse leveling property.

[0080] In addition, when the protective film compositions further contain the polyvinylpyrrolidone-based water-soluble resin (A-2) with a K value of 5 to 70

(Examples 8 to 13), the leveling property of the protective film compositions may be further improved.

[0081] Based on the above, the protective film composition of the invention contains the polyvinylpyrrolidone-based water-soluble resin (A-1) with a K value of 75 to 150 and the laser light absorbing agent (B), and therefore the technical issue of worse leveling property in the prior art may be alleviated.

[0082] Although the invention has been described with reference to the above embodiments, it will be apparent to one of ordinary skill in the art that modifications to the described embodiments may be made without departing from the spirit of the disclosure. Accordingly, the scope of the disclosure is defined by the attached claims not by the above detailed descriptions.

CLAIMS

WHAT IS CLAIMED IS:

[Claim 1] A protective film composition, comprising:

a water-soluble resin (A);

a laser light absorbing agent (B); and

a solvent (C), wherein

the water-soluble resin (A) comprises a polyvinylpyrrolidone-based water-soluble resin (A-1) and a polyvinylpyrrolidone-based water-soluble resin (A-2),

a K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 75 to 150,

and

a K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 5 to 70,

based on 100 parts by weight of the water-soluble resin (A),

a usage amount of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 25 parts by weight to 65 parts by weight,

a usage amount of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 35 parts by weight to 75 parts by weight.

[Claim 2] The protective film composition of claim 1, wherein

the K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 80 to 140.

[Claim 3] The protective film composition of claim 1, wherein

the K value of the polyvinylpyrrolidone-based water-soluble resin (A-1) is 80 to 130.

[Claim 4] The protective film composition of claim 1, wherein

the K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 10 to 65.

[Claim 5] The protective film composition of claim 1, wherein

the K value of the polyvinylpyrrolidone-based water-soluble resin (A-2) is 15 to 65.

[Claim 6] The protective film composition of claim 1, wherein

based on 100 parts by weight of the water-soluble resin (A),

a usage amount of the laser light absorbing agent (B) is 1 part by weight to 30 parts by weight,

a usage amount of the solvent (C) is 500 parts by weight to 3000 parts by weight.

[Claim 7] The protective film composition of any one of claims 1 to 6, which is used for laser cutting.

[Claim 8] A manufacturing method of a semiconductor device, comprising:

a step of applying the protective film composition of any one of claims 1 to 6 on a substrate to form a protective layer;

a step of irradiating the substrate with a laser light through the protective layer to perform laser cutting; and

a step of washing the substrate with water after laser cutting and removing the protective layer from the substrate.

[Claim 9] A laser cutting method, comprising:

a step of applying the protective film composition of any one of claims 1 to 6 on a substrate to form a protective layer;

a step of irradiating the substrate with a laser light through the protective layer to perform laser cutting; and

a step of washing the substrate with water after laser cutting and removing the protective layer from the substrate.