

DESCRIPTION

Title of Invention

FILM-SHAPED ADHESIVE, ADHESIVE SHEET,
SEMICONDUCTOR DEVICE, AND PRODUCTION METHOD FOR
SEMICONDUCTOR DEVICE

Technical Field

[0001] The present invention relates to a film-shaped adhesive, an adhesive sheet, a semiconductor device, and a method for producing a semiconductor device.

Background Art

[0002] In recent years, stacked MCPs (Multi Chip Packages) in which semiconductor elements (semiconductor chips) are stacked in multiple stages have been popularized, and stacked MCPs are mounted as memory semiconductor packages for mobile telephones and mobile audio devices, and the like. Furthermore, along with multifunctioning of mobile telephones and the like, speed increase, density increase, high integration, and the like of semiconductor packages have also been promoted. Concomitantly with this, attempts have been made to increase speed by using copper as a wiring material for semiconductor chip circuits. Furthermore, from the viewpoints of enhancing the reliability of connection to complicated mounting boards and promoting heat rejection from semiconductor packages, lead frames and the like that are composed of copper are in use.

[0003] However, since copper has a characteristic of being easily corrodible, and the coating materials for securing insulation properties of circuit surfaces also tend to be simplified from the viewpoint of cost

reduction, it tends to become difficult to secure electrical characteristics of semiconductor packages. Particularly, in semiconductor packages obtained by stacking semiconductor chips in multiple stages, there is a tendency that copper ions generated due to corrosion migrate through the inside of adhesive, and a loss of electrical signals within semiconductor chips or between a semiconductor chip and another semiconductor chip easily occurs.

[0004] Furthermore, from the viewpoint of high functioning, semiconductor elements are connected to complicated mounting boards in many cases, and thus, lead frames composed of copper tend to be preferred in order to enhance the connection reliability. Even in such a case, a loss of electrical signals caused by copper ions generated from a lead frame may bring a problem.

[0005] Furthermore, with regard to semiconductor packages that use members composed of copper, there is a high possibility that copper ions may be generated from those members and cause electrical failure, and sufficient HAST resistance may not be obtained.

[0006] From the viewpoint of preventing a loss of electrical signals or the like, an investigation has been conducted on adhesives that scavenge copper ions generated inside a semiconductor package. For example, Patent Literature 1 discloses an adhesive sheet for semiconductor device production, the adhesive sheet having a thermoplastic resin that has an epoxy group and does not have a carboxyl group, and an organic complex-forming compound that has a heterocyclic compound containing a tertiary nitrogen atom as a ring atom and forms a complex with a cation.

[0007] However, conventional adhesives are not satisfactory from the viewpoint of suppressing permeation of copper ion in the adhesive, and there is still room for improvement.

Citation List

5 Patent Literature

[0008] Patent Literature 1: JP No. 2013-026566

Summary of Invention

Technical Problem

10 [0009] Thus, a main object of the present invention is to provide a film-shaped adhesive in which permeation of copper ions within the adhesive can be sufficiently suppressed, and which has superior adhesive power.

Solution to Problem

15 [0010] The inventors of the present invention conducted a thorough investigation, and they found that when a specific acrylic rubber and a specific component are incorporated into a film-shaped adhesive, permeation of copper ions within the adhesive can be sufficiently suppressed, and superior adhesive power is obtained, thus completing the present invention.

20 [0011] According to an aspect of the present invention, there is provided a film-shaped adhesive for adhering a semiconductor element to a support member for mounting the semiconductor element, the film-shaped adhesive contains a heat-curable resin, a curing agent, an acrylic rubber, and a heterocyclic compound, wherein in the infrared
25 absorption spectrum of the acrylic rubber, when the height of an absorption peak originating from stretching vibration of a carbonyl

group is designated as P_{CO} , and the height of a peak originating from stretching vibration of a nitrile group is designated as P_{CN} , P_{CO} and P_{CN} satisfy the condition of the following Formula (1), and the thickness of the film-shaped adhesive is 50 μm or less:

5
$$P_{CN}/P_{CO} < 0.070 \quad (1).$$

[0012] Satisfying the condition of Formula (1) means that in the acrylic rubber, the quantity of a constituent unit derived from acrylonitrile is small (or such a constituent unit is not included). By using an acrylic rubber in which the quantity of a constituent unit derived from
10 acrylonitrile is small (or such a constituent unit is not included), permeation of copper ions within the adhesive can be sufficiently suppressed. The reason why such an effect is provided is not necessarily clearly known; however, the present inventors speculate that it is because since the quantity of nitrile groups of acrylonitrile, which is
15 liable to form a complex with a copper ion (complex stability constant is high), is small (or no nitrile group is included), uptake of copper ions by the film-shaped adhesive is diminished, and consequently, permeation of copper ions within the adhesive is suppressed. Furthermore, there is a tendency that an acrylic rubber in which the quantity of a constituent
20 unit derived from acrylonitrile is small (or such a constituent unit is not included) does not easily form a phase-separated structure, and a possibility that the difficulty of adopting a phase-separated structure may be affecting the suppression of permeation of copper ions within the adhesive can also be considered.

25 [0013] As the film-shaped adhesive contains a heterocyclic compound, permeation of copper ions within the adhesive is sufficiently

suppressed, and also, the adhesive power tends to be superior. The heterocyclic compound may be an aromatic compound having three or more nitrogen atoms. The heterocyclic compound may be at least one selected from the group consisting of a triazole compound and a tetrazole compound. The content of the heterocyclic compound may be 0.01 to 2 parts by mass with respect to 100 parts by mass of the total mass of the heat-curable resin, the curing agent, and the acrylic rubber.

[0014] The film-shaped adhesive may further contain an inorganic filler, and the average particle size of the inorganic filler may be 1 μm or less.

[0015] According to another aspect of the present invention, there is provided an adhesive sheet comprising a base material and the above-described film-shaped adhesive provided on one surface of the base material. The base material may be a dicing tape.

[0016] According to still another aspect of the present invention, there is provided a semiconductor device comprising a semiconductor element; a support member for mounting the semiconductor element; and an adhesive member provided between the semiconductor element and the support member and adhering the semiconductor element to the support member, the adhesive member being a cured product of the above-mentioned film-shaped adhesive. The support member may include a member composed of copper.

[0017] According to still another aspect of the present invention, there is provided a method for producing a semiconductor device, the method comprising a step of adhering a semiconductor element to a support member using the above-mentioned film-shaped adhesive.

[0018] According to still another aspect of the present invention, there is provided a method for producing a semiconductor device, the method comprising a step of sticking the film-shaped adhesive of the above-mentioned adhesive sheet to a semiconductor wafer; a step of
5 cutting the semiconductor wafer having the film-shaped adhesive stuck thereto to produce a plurality of individually divided film-shaped adhesive-attached semiconductor elements; and a step of adhering each of the film-shaped adhesive-attached semiconductor elements to a support member. The method for producing a semiconductor device
10 may further comprise a step of heating the film-shaped adhesive-attached semiconductor element adhered to the support member, using a reflow furnace.

Advantageous Effects of Invention

[0019] According to the present invention, there is provided a
15 film-shaped adhesive in which permeation of copper ions within the adhesive can be sufficiently suppressed, and which has superior adhesive power. Furthermore, according to the present invention, an adhesive sheet and a semiconductor device, which use such a film-shaped adhesive, are provided. In addition, according to the
20 present invention, a method for producing a semiconductor device using a film-shaped adhesive or an adhesive sheet is provided.

Brief Description of Drawings

[0020] FIG. 1 is a schematic cross-sectional view illustrating an
embodiment of a film-shaped adhesive.

25 FIG. 2 is a schematic cross-sectional view illustrating an embodiment of an adhesive sheet.

FIG. 3 is a schematic cross-sectional view illustrating another embodiment of the adhesive sheet.

FIG. 4 is a schematic cross-sectional view illustrating another embodiment of the adhesive sheet.

5 FIG. 5 is a schematic cross-sectional view illustrating another embodiment of the adhesive sheet.

FIG. 6 is a schematic cross-sectional view illustrating an embodiment of a semiconductor device.

10 FIG. 7 is a schematic cross-sectional view illustrating another embodiment of the semiconductor device.

Description of Embodiments

[0021] Hereinafter, embodiments of the present invention will be described with appropriate reference to the drawings. However, the present invention is not intended to be limited to the following
15 embodiments. In the following embodiments, constituent elements of the embodiments (also including steps and the like) are not essential unless particularly stated otherwise. The sizes of the constituent elements in each of the diagrams are conceptual, and the relative relationship between the sizes of the constituent elements is not limited
20 to the relationship as illustrated in each diagram.

[0022] The same also applies to the numerical values and ranges thereof in the present specification, and the present invention is not intended to be limited. A numerical value range expressed using the term "to" in the present specification represents a range including the
25 numerical values described before and after the term "to" as the minimum value and the maximum value, respectively. With regard to

the numerical value range described stepwise in the present specification, the upper limit value or the lower limit value described in one numerical value range may be replaced with the upper limit value or the lower limit value of another stepwise numerical value range described. Furthermore, with regard to a numerical value ranges described in the present specification, the upper limit value or the lower limit value of the numerical value range may be replaced with the values described in Examples.

[0023] According to the present specification, (meth)acrylate means acrylate or methacrylate corresponding thereto. The same also applies to other similar expressions such as a (meth)acryloyl group and a (meth)acrylic copolymer.

[0024] A film-shaped adhesive according to an embodiment is a film-shaped adhesive for adhering a semiconductor element to a support member for mounting the semiconductor element, the film-shaped adhesive containing: (A) a heat-curable resin, (B) a curing agent, (C) an acrylic rubber, and (D) a heterocyclic compound, wherein in the infrared absorption spectrum of the (C) acrylic rubber, when the height of an absorption peak originating from stretching vibration of a carbonyl group is designated as P_{CO} , and the height of a peak originating from stretching vibration of a nitrile group is designated as P_{CN} , P_{CO} and P_{CN} satisfy the condition of the following Formula (1), and the thickness of the film-shaped adhesive is 50 μm or less:

$$P_{CN}/P_{CO} < 0.070 \quad (1).$$

[0025] The film-shaped adhesive can be obtained by molding an adhesive composition containing: (A) a heat-curable resin, (B) a curing

agent, (C) an acrylic rubber, and (D) a heterocyclic compound, into a film shape. The film-shaped adhesive and the adhesive composition may be an adhesive and a composition, respectively, which can go through a semi-cured (stage B) state and enter a completely cured (stage C) state after a curing treatment.

[0026] Component (A): Heat-curable resin

The component (A) may be an epoxy resin from the viewpoint of adhesiveness. Regarding the epoxy resin, any resin having an epoxy group in the molecule can be used without particular limitations. Examples of the epoxy resin include a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a bisphenol S type epoxy resin, a phenol novolac type epoxy resin, a cresol novolac type epoxy resin, a bisphenol A novolac type epoxy resin, a bisphenol F novolac type epoxy resin, a stilbene type epoxy resin, a triazine skeleton-containing epoxy resin, a fluorene skeleton-containing epoxy resin, a triphenolmethane type epoxy resin, a biphenyl type epoxy resin, a xylylene type epoxy resin, a biphenyl aralkyl type epoxy resin, a naphthalene type epoxy resin, a polyfunctional phenol, and a diglycidyl ether compound of a polycyclic aromatic compound such as anthracene. These may be used singly or in combination of two or more kinds thereof. Among these, the component (A) may be a cresol novolac type epoxy resin, a bisphenol F type epoxy resin, or a bisphenol A type epoxy resin, from the viewpoints of tackiness, pliability, and the like of a film.

[0027] The epoxy equivalent of the epoxy resin is not particularly limited; however, the epoxy equivalent may be 90 to 300 g/eq, 110 to 290 g/eq, or 110 to 290 g/eq. When the epoxy equivalent of the epoxy

resin is in such a range, there is a tendency that fluidity can be secured while maintaining the bulk strength of the film-shaped adhesive.

[0028] Component (B): Curing agent

5 The component (B) may be a phenolic resin that can serve as a curing agent for an epoxy resin. Regarding the phenolic resin, any resin having a phenolic hydroxyl group in the molecule can be used without particular limitations. Examples of the phenolic resin include a novolac type phenolic resin obtainable by condensing or co-condensing a phenol such as phenol, cresol, resorcin, catechol, 10 bisphenol A, bisphenol F, phenylphenol, or aminophenol, and/or a naphthol such as α -naphthol, β -naphthol, or dihydroxynaphthalene, with a compound having an aldehyde group, such as formaldehyde, in the presence of an acidic catalyst; a phenol aralkyl resin synthesized from a phenol and/or a naphthol, such as allylated bisphenol A, allylated 15 bisphenol F, allylated naphthalenediol, phenol novolac, or phenol, and dimethoxy-para-xylene or bis(methoxymethyl)biphenyl; and a naphthol aralkyl resin. These may be used singly or in combination of two or more kinds thereof. Among these, the phenolic resin may be a phenol aralkyl resin or a naphthol aralkyl resin.

20 [0029] The hydroxyl group equivalent of the phenolic resin may be 70 g/eq or more or 70 to 300 g/eq. When the hydroxyl group equivalent of the phenolic resin is 70 g/eq or more, the storage modulus of the film tends to be further enhanced, and when the hydroxyl group equivalent is 300 g/eq or less, inconvenience caused by the occurrence of foaming, 25 outgassing, and the like can be prevented.

[0030] From the viewpoint of curability, the ratio between the epoxy

equivalent of the epoxy resin and the hydroxyl group equivalent of the phenolic resin (epoxy equivalent of epoxy resin/hydroxyl group equivalent of phenolic resin) may be 0.30/0.70 to 0.70/0.30, 0.35/0.65 to 0.65/0.35, 0.40/0.60 to 0.60/0.40, or 0.45/0.55 to 0.55/0.45. When this equivalent ratio is 0.30/0.70 or more, more sufficient curability tends to be obtained. When this equivalent ratio is 0.70/0.30 or less, viscosity can be prevented from excessively increasing, and more sufficient fluidity can be obtained.

[0031] The total content of the component (A) and the component (B) may be 5 to 50 parts by mass, 10 to 40 parts by mass, or 15 to 30 parts by mass, with respect to 100 parts by mass of the total mass of the component (A), component (B), and component (C). When the total content of the component (A) and the component (B) is 5 parts by mass or more, the elastic modulus tends to be increased by crosslinking. When the total content of the component (A) and the component (B) is 50 parts by mass or less, there is a tendency that film handleability can be retained.

[0032] Component (C): Acrylic rubber

The component (C) is a rubber having a constituent unit derived from a (meth)acrylic acid ester as a main component. The content of the constituent unit derived from a (meth)acrylic acid ester in the component (C) may be, for example, 70% by mass or more, 80% by mass or more, or 90% by mass or more, based on the total amount of the constituent units. The component (C) may be a rubber including a constituent unit derived from a (meth)acrylic acid ester having a crosslinkable functional group such as an epoxy group, an alcoholic or

phenolic hydroxyl group, or a carboxyl group. The component (C) may be a rubber including a constituent unit derived from acrylonitrile to the extent that the condition of Formula (1) that will be described below is satisfied; however, from the viewpoint of being capable of further suppressing permeation of copper ions within the adhesive and having superior embeddability, the component (C) may be a rubber that does not include a constituent unit derived from acrylonitrile.

[0033] With regard to the infrared absorption spectrum of the component (C), when the height of an absorption peak originating from stretching vibration of a carbonyl group is designated as P_{CO} , and the height of a peak originating from stretching vibration of a nitrile group is designated as P_{CN} , P_{CO} and P_{CN} satisfy the condition of the following Formula (1):

$$P_{CN}/P_{CO} < 0.070 \quad (1).$$

[0034] Here, the carbonyl group mainly originates from a (meth)acrylic acid ester, which is a constituent unit, and the nitrile group mainly originates from acrylonitrile, which is a constituent unit. Incidentally, the height (P_{CO}) of an absorption peak originating from stretching vibration of a carbonyl group and the height (P_{CN}) of a peak originating from stretching vibration of a nitrile group have meanings as defined in Examples.

[0035] A small value of P_{CN}/P_{CO} means that the quantity of the constituent unit derived from acrylonitrile is small in the component (C). Therefore, a component (C) that does not include a constituent unit derived from acrylonitrile can theoretically satisfy the condition of Formula (1).

[0036] The value of P_{CN}/P_{CO} is less than 0.070 and may be 0.065 or less, 0.060 or less, 0.055 or less, 0.050 or less, 0.040 or less, 0.030 or less, 0.020 or less, or 0.010 or less. When the value of P_{CN}/P_{CO} is less than 0.070, permeation of copper ions within the adhesive can be sufficiently suppressed. Furthermore, as the value of P_{CN}/P_{CO} becomes smaller, permeation of copper ions within the adhesive can be more sufficiently suppressed. Moreover, as the value of P_{CN}/P_{CO} becomes smaller, since the cohesive force of the component (C) is decreased, embeddability also tends to become superior.

[0037] The glass transition temperature (T_g) of the component (C) may be -50°C to 50°C or -30°C to 30°C . When the T_g of the component (C) is -50°C or higher, there is a tendency that pliability of the adhesive can be prevented from excessively increasing. As a result, it is easy to cut the film-shaped adhesive during wafer dicing, and the occurrence of burring can be prevented. When the T_g of the component (C) is 50°C or lower, there is a tendency that a decrease in pliability of the adhesive can be suppressed. As a result, when the film-shaped adhesive is stuck to a wafer, it tends to become easy to sufficiently embed voids. Furthermore, it is possible to prevent chipping of the wafer at the time of dicing, which is caused by a decrease in the adhesive power. Here, the glass transition temperature (T_g) means the value measured using a DSC (thermal differential scanning calorimeter) (for example, manufactured by Rigaku Corporation, Thermo Plus 2).

[0038] The weight average molecular weight (M_w) of the component (C) may be 100000 to 3000000 or 200000 to 2000000. When the M_w of the component (C) is in such a range, the film-forming property, and

strength, flexibility, tackiness, and the like in a film form can be appropriately controlled, and at the same time, excellent reflow characteristics are obtained so that embeddability can be enhanced. Here, the Mw means the value measured by gel permeation chromatography (GPC) and converted using a calibration curve produced with polystyrene standards.

[0039] Examples of a commercially available product of the component (C) that does not include a constituent unit derived from acrylonitrile include KH-CT-865 (manufactured by Hitachi Chemical Co., Ltd.).

[0040] The content of the component (C) may be 50 to 95 parts by mass, 60 to 90 parts by mass, or 70 to 85 parts by mass, with respect to 100 parts by mass of the total mass of the component (A), component (B), and component (C). When the content of the component (C) is in such a range, there is a tendency that permeation of copper ions within the adhesive can be more sufficiently suppressed.

[0041] Component (D): Heterocyclic compound

The film-shaped adhesive tends to have the permeation of copper ions within the adhesive sufficiently suppressed and to have superior adhesive power, by containing the component (D). The component (D) may be an aromatic compound having three or more nitrogen atoms and may be at least one selected from the group consisting of a triazole compound and a tetrazole compound.

[0042] Examples of the triazole compound include benzotriazole, benzotriazole-1-acetonitrile, benzotriazole-5-carboxylic acid, benzotriazole-1-methanol, carboxybenzotriazole, 3-mercaptopotriazole, 5-mercaptopotriazole; and amino group substitution products of the

above-described compounds. The triazole compound may be benzotriazole or 3-mercaptopotriazole.

[0043] Examples of the tetrazole compound include 5-methyltetrazole, 5-aminotetrazole, 1-methyl-5-aminotetrazole, 1-methyl-5-mercapto-1H-tetrazole, and 1-carboxymethyl-5-aminotetrazole. The tetrazole compound may be 5-methyltetrazole or 5-aminotetrazole.

[0044] The content of the component (D) may be 0.01 to 2 parts by mass with respect to 100 parts by mass of the total mass of the component (A), component (B), and component (C). When the content of the component (D) is in such a range, the film-shaped adhesive tends to be superior from the viewpoint of adhesive power. The content of the component (D) may be 0.03 parts by mass or more, 0.05 parts by mass or more, 0.1 parts by mass or more, or 0.3 parts by mass or more. The content of the component (D) may be 2 parts by mass or less, 1.8 parts by mass or less, 1.5 parts by mass or less, or 1.2 parts by mass or less.

[0045] The film-shaped adhesive (adhesive composition) may further contain: (E) an inorganic filler, (F) a coupling agent, (G) a curing accelerator, and the like.

[0046] Component (E): Inorganic filler

Examples of the component (E) include aluminum hydroxide, magnesium hydroxide, calcium carbonate, magnesium carbonate, calcium silicate, magnesium silicate, calcium oxide, magnesium oxide, aluminum oxide, aluminum nitride, aluminum borate whiskers, boron nitride, and silica. These may be used singly or in combination of two

or more kinds thereof. Among these, the component (E) may be silica from the viewpoint of adjusting the melt viscosity.

[0047] The average particle size of the component (E) may be 1 μm or less. The average particle size of the component (E) may be 0.01 to 1 μm , 0.01 to 0.8 μm , 0.03 to 0.5 μm , 0.03 to 0.3 μm , or 0.03 to 0.1 μm , from the viewpoint of fluidity. Here, the average particle size means a value that is determined by converting from the BET specific surface area. As the average particle size of the component (E) becomes smaller, permeation of copper ions within the adhesive can be even more sufficiently suppressed.

[0048] The shape of the component (E) is not particularly limited; however, the shape may be a spherical shape.

[0049] The content of the component (E) may be 0.1 to 50 parts by mass, 0.1 to 30 parts by mass, or 0.1 to 20 parts by mass, with respect to 100 parts by mass of the total mass of the component (A), component (B), and component (C).

[0050] Component (F): Coupling agent

The component (F) may be a silane coupling agent. Examples of the silane coupling agent include γ -ureidopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, 3-phenylaminopropyltrimethoxysilane, and 3-(2-aminoethyl)aminopropyltrimethoxysilane. These may be used singly or in combination of two or more kinds thereof.

[0051] Component (G): Curing accelerator

The component (G) is not particularly limited, and any agent that is generally used can be used. Examples of the component (G)

include an imidazole and derivatives thereof, an organic phosphorus-based compound, a secondary amine, a tertiary amine, and a quaternary ammonium salt. These may be used singly or in combination of two or more kinds thereof. Among these, from the viewpoint of reactivity, the component (G) may be an imidazole and derivatives thereof.

[0052] Examples of the imidazole include 2-methylimidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, and 1-cyanoethyl-2-methylimidazole. These may be used singly or in combination of two or more kinds thereof.

[0053] The film-shaped adhesive (adhesive composition) may further contain other components. Examples of the other components include a pigment, an ion trapping agent, and an oxidation inhibitor.

[0054] The content of the component (F), component (G), and other components may be 0 to 30 parts by mass with respect to 100 parts by mass of the total mass of the component (A), component (B), and component (C).

[0055] FIG. 1 is a schematic cross-sectional view illustrating an embodiment of the film-shaped adhesive. The film-shaped adhesive 1 (adhesive film) illustrated in FIG. 1 is a product obtained by molding an adhesive composition into a film form. The film-shaped adhesive 1 may be in a semi-cured (stage B) state. Such a film-shaped adhesive 1 can be formed by applying an adhesive composition on a support film. In the case of using a varnish of an adhesive composition (adhesive varnish), the film-shaped adhesive 1 can be formed by mixing the component (A), component (B), component (C), component (D), and

other optionally added components in a solvent, mixing or kneading the mixed liquid to prepare an adhesive varnish, applying the adhesive varnish on a support film, and removing the solvent by heating and drying.

5 [0056] The support film is not particularly limited so long as the support film withstands the above-described heating and drying; however, the support film may be, for example, a polyester film, a polypropylene film, a polyethylene terephthalate film, a polyimide film, a polyetherimide film, a polyether naphthalate film, a
10 polymethylpentene film, or the like. The support film may be a multilayer film combining two or more kinds or may be a film having the surface treated with a mold release agent such as a silicone-based agent or a silica-based agent, or the like. The thickness of the support film may be, for example, 10 to 200 μm or 20 to 170 μm .

15 [0057] Mixing or kneading can be carried out using conventional dispersing machines such as a stirrer, a Raikai mixer, a three-roll, and a ball mill, by appropriately combining these.

[0058] The solvent to be used for the preparation of the adhesive varnish is not limited so long as the solvent can uniformly dissolve,
20 knead, or disperse various components, and conventionally known solvents can be used. Examples of such a solvent include ketone-based solvents such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone; dimethylformamide, dimethylacetamide, N-methylpyrrolidone, toluene, and xylene. The
25 solvent may be methyl ethyl ketone, cyclohexanone, or the like from the viewpoints of the drying speed and the price.

[0059] Regarding the method of applying the adhesive varnish on a support film, any known method can be used, and examples include a knife coating method, a roll coating method, a spray coating method, a gravure coating method, a bar coating method, and a curtain coating method. The conditions for heating and drying are not particularly limited so long as they are conditions in which the solvent used is sufficiently volatilized; however, heating and drying can be carried out by heating at 50°C to 150°C for 1 to 30 minutes.

[0060] When the thickness of the film-shaped adhesive is 50 μm or less, since the distance between a semiconductor element and a support member for mounting the semiconductor element is shortened, inconvenience caused by copper ions tends to occur easily. With regard to the film-shaped adhesive according to the present embodiment, since it is possible to sufficiently suppress permeation of copper ions within the adhesive, the thickness of the film-shaped adhesive can be adjusted to 50 μm or less. The thickness of the film-shaped adhesive 1 may be 40 μm or less, 30 μm or less, 20 μm or less, or 15 μm or less. The lower limit of the thickness of the film-shaped adhesive 1 is not particularly limited; however, the lower limit can be adjusted to, for example, 1 μm or more.

[0061] The copper ion permeation time of the film-shaped adhesive 1 in a semi-cured (stage B) state may be longer than 80 minutes and may also be 85 minutes or longer, 90 minutes or longer, 100 minutes or longer, 150 minutes or longer, 200 minutes or longer, or 250 minutes or longer. As the copper ion permeation time is longer than 80 minutes, even in a case in which defects such as insufficient curing occur during

the production of a semiconductor device, it is anticipated that inconvenience caused by copper ions is less likely to occur.

[0062] The copper ion permeation time of the film-shaped adhesive 1 in a completely cured (stage C) state (that is, a cured product of the film-shaped adhesive) may be longer than 100 minutes and may also be 120 minutes or longer, 140 minutes or longer, 160 minutes or longer, 180 minutes or longer, 200 minutes or longer, or 250 minutes or longer. Inconvenience caused by copper ions tends to easily occur during a high temperature treatment such as a reflow process. Therefore, as the completely cured (stage C) state lasts longer than 100 minutes, it is anticipated that inconvenience caused by copper ions is less likely to occur.

[0063] FIG. 2 is a schematic cross-sectional view illustrating an embodiment of an adhesive sheet. The adhesive sheet 100 illustrated in FIG. 2 comprises a base material 2 and a film-shaped adhesive 1 provided on the base material 2. FIG. 3 is a schematic cross-sectional view illustrating another embodiment of the adhesive sheet. The adhesive sheet 110 illustrated in FIG. 3 comprises a base material 2; a film-shaped adhesive 1 provided on the base material 2; and a cover film 3 provided on a surface of the film-shaped adhesive 1, the surface being on the opposite side of the base material 2.

[0064] The base material 2 is not particularly limited; however, the base material 2 may be a base material film. The base material film may be a film similar to the above-mentioned support film.

[0065] The cover film 3 is used to prevent any damage or contamination of the film-shaped adhesive and may be, for example, a

polyethylene film, a polypropylene film, a surface peeling agent-treated film, or the like. The thickness of the cover film 3 may be, for example, 15 to 200 μm or 70 to 170 μm .

5 [0066] The adhesive sheets 100 and 110 can be formed by applying an adhesive composition on a base material film, similarly to the above-described method for forming a film-shaped adhesive. The method for applying an adhesive composition on a base material 2 may be similar to the above-described method of applying an adhesive composition on a support film.

10 [0067] The adhesive sheet 110 can be obtained by further laminating the cover film 3 on the film-shaped adhesive 1.

[0068] The adhesive sheets 100 and 110 may also be formed using a film-shaped adhesive that has been produced in advance. In this case, the adhesive sheet 100 can be formed by performing lamination under
15 predetermined conditions (for example, room temperature (20°C) or a heated state) using a roll laminator, a vacuum laminator, or the like. From the viewpoint that the adhesive sheet 100 can be continuously produced and has excellent efficiency, the adhesive sheet 100 may also be formed using a roll laminator in a heated state.

20 [0069] Another embodiment of the adhesive sheet is a dicing-die bonding integrated adhesive sheet, in which the base material 2 is a dicing tape. When a dicing-die bonding integrated adhesive sheet is used, since the process of lamination on a semiconductor wafer is performed once, efficient implementation of operation is enabled.

25 [0070] Examples of the dicing tape include plastic films such as a polytetrafluoroethylene film, a polyethylene terephthalate film, a

polyethylene film, a polypropylene film, a polymethylpentene film, and a polyimide film. Furthermore, the dicing tape may have been subjected to a surface treatment such as primer coating, a UV treatment, a corona discharge treatment, a polishing treatment, or an etching treatment, as necessary. The dicing tape may have tacky adhesiveness. Such a dicing tape may be a product obtained by imparting tacky adhesiveness to the above-mentioned plastic film and may be a product obtained by providing a tacky adhesive layer on one surface of the above-mentioned plastic film. The tacky adhesive layer may be any of a pressure-sensitive type layer or a radiation-curable type layer and is not particularly limited so long as the tacky adhesive layer has sufficient tacky adhesive force that does not allow scattering of semiconductor elements during dicing and has low tacky adhesive force to the extent that semiconductor elements are not impaired during a subsequent pickup process for semiconductor elements, and any conventionally known tacky adhesive layer can be used.

[0071] The thickness of the dicing tape may be 60 to 150 μm or 70 to 130 μm , from the viewpoints of economic efficiency and film handleability.

[0072] Examples of such a dicing-die bonding integrated adhesive sheet include an adhesive sheet having the configuration illustrated in FIG. 4 and an adhesive sheet having the configuration illustrated in FIG. 5. FIG. 4 is a schematic cross-sectional view illustrating another embodiment of the adhesive sheet. FIG. 5 is a schematic cross-sectional view illustrating another embodiment of the adhesive sheet. The adhesive sheet 120 illustrated in FIG. 4 comprises a dicing

tape 7, a tacky adhesive layer 6, and a film-shaped adhesive 1 in this order. The adhesive sheet 130 illustrated in FIG. 5 comprises a dicing tape 7 and a film-shaped adhesive 1 provided on the dicing tape 7.

5 [0073] The adhesive sheet 120 can be obtained by, for example, providing a tacky adhesive layer 6 on a dicing tape 7 and further laminating a film-shaped adhesive 1 on the tacky adhesive layer 6. The adhesive sheet 130 can be obtained by, for example, sticking a dicing tape 7 and a film-shaped adhesive 1 together.

10 [0074] The film-shaped adhesive and the adhesive sheet may be used for the production of a semiconductor device and may be used for the production of a semiconductor device, the production including a step of sticking a film-shaped adhesive and a dicing tape to a semiconductor wafer or already fragmented semiconductor elements (semiconductor chips) at 0°C to 90°C, subsequently obtaining film-shaped
15 adhesive-attached semiconductor elements by dividing the assembly with a rotating blade, a laser, or by extension, and then adhering one of the film-shaped adhesive-attached semiconductor elements onto an organic substrate, a lead frame, or another semiconductor element.

20 [0075] Examples of the semiconductor wafer include single crystal silicon, polycrystalline silicon, various ceramics, and compound semiconductors such as gallium arsenide.

[0076] The film-shaped adhesive and the adhesive sheet can be used as adhesives for die bonding for sticking together a semiconductor element such as IC or LSI and a lead frame such as an alloy 42 lead frame or a
25 copper lead frame; a film of a plastic such as a polyimide resin or an epoxy resin; a product obtained by impregnating a base material such as

a nonwoven glass fabric with a plastic such as a polyimide resin or an epoxy resin and curing the resultant; a support member for semiconductor mounting, formed of a ceramic such as alumina, or the like; or the like.

5 [0077] The film-shaped adhesive and the adhesive sheet are suitably used also as adhesives for adhering a semiconductor element and another semiconductor element in a Stacked-PKG having a structure in which a plurality of semiconductor elements are stacked. In this case, one of the semiconductor elements serves as a support member for
10 mounting a semiconductor element.

[0078] The film-shaped adhesive and the adhesive sheet can also be used as, for example, protective sheets for protecting the back surface of semiconductor elements in a flip chip type semiconductor device, sealing sheets for sealing between the surface of semiconductor
15 elements of a flip chip type semiconductor device and an adherend, or the like.

[0079] A semiconductor device produced using a film-shaped adhesive will be specifically described using the drawings. Incidentally, in recent years, semiconductor devices having various structures have been
20 proposed, and the use application of the film-shaped adhesive according to the present embodiment is not limited to the semiconductor device having the structure described below.

[0080] FIG. 6 is a schematic cross-sectional view illustrating an embodiment of a semiconductor device. The semiconductor device
25 200 illustrated in FIG. 6 comprises a semiconductor element 9; a support member 10 for mounting the semiconductor element 9; and an adhesive

member (cured product 1c of the film-shaped adhesive) provided between the semiconductor element 9 and the support member 10 and adhering the semiconductor element 9 to the support member 10. A connection terminal (not illustrated in the diagram) of the semiconductor element 9 is electrically connected to an external connection terminal (not illustrated in the diagram) through a wire 11 and is sealed by a sealing material 12.

[0081] FIG. 7 is a schematic cross-sectional view illustrating another embodiment of the semiconductor device. In the semiconductor device 210 illustrated in FIG. 7, a semiconductor element 9a of a first stage is adhered to a support member 10 having a terminal 13 formed thereon, by an adhesive member (cured product 1c of the film-shaped adhesive), and a semiconductor element 9b of a second stage is further adhered onto the semiconductor element 9a of the first stage by an adhesive member (cured product 1c of the film-shaped adhesive). The connection terminals (not illustrated in the diagram) of the semiconductor element 9a of the first stage and the semiconductor element 9b of the second stage are electrically connected to external connection terminals through a wire 11 and are sealed by a sealing material 12. As such, the film-shaped adhesive according to the present embodiment can also be suitably used in a semiconductor device having a structure in which a plurality of semiconductor elements are stacked.

[0082] The semiconductor devices (semiconductor packages) illustrated in FIG. 6 and FIG. 7 can be obtained by, for example, interposing a film-shaped adhesive between a semiconductor element and a support

member or between a semiconductor element and another semiconductor element, adhering the two by subjecting those to heating and pressure-bonding, and subsequently performing a wire bonding step, a sealing step using a sealing material, a heating and melting step including reflow soldering, and the like, as necessary. The heating temperature in the heating and pressure-bonding step is usually 20°C to 250°C, the load is usually 0.1 to 200 N, and the heating time is usually between 0.1 to 300 seconds.

[0083] Regarding the method of interposing the film-shaped adhesive between a semiconductor element and a support member or between a semiconductor element and another semiconductor element, as described above, a method of producing a film-shaped adhesive-attached semiconductor element in advance and then sticking the semiconductor element to a support member or another semiconductor element is preferred.

[0084] The support member may include a member composed of copper. In the semiconductor device according to the present embodiment, since a semiconductor element and a support member are adhered by a cured product 1c of the film-shaped adhesive, even in a case in which a member composed of copper is used as a constituent member of the semiconductor device, the influence of copper ions generated from the member can be reduced, and the occurrence of any electrical inconvenience caused by copper ions can be sufficiently suppressed.

[0085] Here, examples of the member composed of copper include a lead frame, a wiring, a wire, and a heat-dissipating material; however,

even when copper is used for any of the members, the influence of copper ions can be reduced.

[0086] Next, an embodiment of the method for producing a semiconductor device in the case of using the dicing-die bonding integrated adhesive sheet illustrated in FIG. 4 will be described. Incidentally, the method for producing a semiconductor device using a dicing-die bonding integrated adhesive sheet is not limited to the method for producing a semiconductor device that will be described below.

[0087] First, a semiconductor wafer is pressure-bonded to a film-shaped adhesive 1 in an adhesive sheet 120 (dicing-die bonding integrated adhesive sheet), and this is adhered and held to be fixed (mounting step). The present step may be carried out by pressing the assembly by a pressing member such as a pressure-bonding roll.

[0088] Next, dicing of the semiconductor wafer is performed. Thereby, the semiconductor wafer is cut out into a predetermined size, and thus a plurality of individually divided film-shaped adhesive-attached semiconductor elements (semiconductor chips) are produced. Dicing can be carried out by, for example, a conventional method from the circuit surface side of the semiconductor wafer. Furthermore, in the present step, for example, a cutting method called full-cut, by which incision up to the dicing tape is performed; a method of dividing the semiconductor wafer by inserting a half-cut incision and cooling and pulling the semiconductor wafer; and a method of cutting the semiconductor wafer using a laser can be employed. The dicing device used for the present step is not particularly limited, and any

conventionally known device can be used.

[0089] In order to detach the semiconductor element adhered and fixed to the dicing-die bonding integrated adhesive sheet, picking up of the semiconductor element is performed. The method for picking up is not particularly limited, and various conventionally known methods can be employed. For example, a method of pushing up individual semiconductor elements by a needle through the dicing-die bonding integrated adhesive sheet side and picking up the pushed semiconductor elements by a pick-up device, and the like may be mentioned.

[0090] Here, picking up is carried out, in a case in which the tacky adhesive layer is a radiation (for example, ultraviolet radiation)-curable type, after the tacky adhesive layer is irradiated with radiation. Thereby, the tacky adhesive force of the tacky adhesive layer to the film-shaped adhesive is decreased, and detachment of the semiconductor element is made easier. As a result, picking up is made possible without damaging the semiconductor element.

[0091] Next, the film-shaped adhesive-attached semiconductor element formed by dicing is adhered to a support member for mounting a semiconductor element, by means of the film-shaped adhesive. Adhesion may be carried out pressure-bonding. The conditions for die-bonding are not particularly limited and can be appropriately set as necessary. Specifically, for example, die-bonding can be carried out at a die-bonding temperature of 80°C to 160°C, a bonding load of 5 to 15 N, and a bonding time in the range of 1 to 10 seconds.

[0092] If necessary, a step of thermally curing the film-shaped adhesive may be provided. By thermally curing the film-shaped adhesive that

adheres the support member and the semiconductor element by the adhesion step, adhesive fixing is enabled more strongly. In the case of performing thermal curing, curing may be achieved by applying pressure at the same time. The heating temperature in the present step
5 can be appropriately changed by the constituent component of the film-shaped adhesive. The heating temperature may be, for example, 60°C to 200°C. Meanwhile, the temperature or pressure may be changed stepwise.

[0093] Next, a wire bonding step of electrically connecting the tip of a
10 terminal part (inner lead) of the support member with an electrode pad on the semiconductor element using a bonding wire is carried out. As the bonding wire, for example, a gold wire, an aluminum wire, a copper wire, or the like is used. The temperature at the time of performing wire bonding may be in the range of 80°C to 250°C or 80°C to 220°C.
15 The heating time may be several seconds to several minutes. Connecting the wire may also be carried out in a state of being heated in the above-described temperature range, by using vibration energy induced by ultrasound and pressure-bonding energy induced by applied pressure in combination.

[0094] Next, a sealing step of sealing the semiconductor element using
20 a sealing resin is carried out. The present step is carried out in order to protect the semiconductor element mounted on the support member or the bonding wire. The present step is carried out by molding a resin for sealing in a mold. The sealing resin may be, for example, an
25 epoxy-based resin. The substrate and residue are embedded by heat and pressure at the time of sealing, and detachment at the adhesion

interface caused by gas bubbles can be prevented.

[0095] Next, in the post-curing step, the sealing resin that has been insufficiently cured in the sealing step is completely cured. Even in a case in which the film-shaped adhesive is not thermally cured in the sealing step, adhesive fixing is enabled by thermally curing the film-shaped adhesive together with curing of the sealing resin in the present step. The heating temperature in the present step can be appropriately set according to the type of the sealing resin, and for example, the heating temperature may be in the range of 165°C to 185°C, while the heating time may be about 0.5 to 8 hours.

[0096] Next, the film-shaped adhesive-attached semiconductor element adhered to the support member is heated using a reflow furnace. In the present step, the resin-sealed semiconductor device may be surface-mounted on the support member. Regarding the method for surface mounting, for example, reflow soldering of supplying solder in advance on the printed wiring board, subsequently heating and melting the solder by warm air or the like, and performing soldering may be mentioned. Examples of the heating method include hot air reflow and infrared reflow. Furthermore, the heating method may be heating the entirety or may be heating a local site. The heating temperature may be, for example, in the range of 240°C to 280°C.

[0097] In the case of laminating semiconductor elements in multiple layers, the thermal history of the wire bonding step and the like increases, and the influence of gas bubbles present at the interface between the film-shaped adhesive and the semiconductor elements on detachment may become serious. However, since the film-shaped

adhesive according to the present embodiment uses a specific acrylic rubber, the cohesive force is decreased, and embeddability tends to be enhanced. Therefore, gas bubbles are not easily entrained into the semiconductor device, gas bubbles can be easily diffused in the sealing step, and detachment caused by gas bubbles at the adhesion interface can be prevented.

Examples

[0098] Hereinafter, the present invention will be specifically described based on Examples; however, the present invention is not intended to be limited to these.

[0099] [Production of film-shaped adhesive]

(Examples and Comparative Examples)

<Preparation of adhesive varnish>

To compositions composed of an epoxy resin as (A) a heat-curable resin, a phenolic resin as (B) a curing agent, and (E) an inorganic filler with the product names and composition ratios (unit: parts by mass) shown in Table 1 and Table 2, cyclohexanone was added, and the mixtures were stirred and mixed. To these mixtures, the (C) acrylic rubbers shown in Table 1 and Table 2 were added and stirred, (D) a heterocyclic compound, (F) a coupling agent, and (G) a curing accelerator as shown in Table 1 and Table 2 were added to the mixtures, the mixtures were stirred until the various components became uniform, and thus adhesive varnishes were prepared. Incidentally, the numerical values of the component (C) and the component (E) shown in Table 1 and Table 2 mean parts by mass of the solid content.

[0100] (A) Heat-curable resin

- (A1) YDCN-700-10 (trade name, manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., o-cresol novolac type epoxy resin, epoxy equivalent: 209 g/eq)
- [0101] (B) Curing agent
- 5 (B1) HE-100C-30 (trade name, manufactured by AIR WATER INC., phenyl aralkyl type phenolic resin, hydroxyl group equivalent: 174 g/eq, softening point 77°C)
- [0102] (C) Acrylic rubber
- (C1) SG-P3 improved product (product obtained by eliminating
- 10 a constituent unit derived from acrylonitrile from the acrylic rubber of SG-P3 (trade name, manufactured by Nagase ChemteX Corp.), weight average molecular weight of acrylic rubber: 600000, theoretical Tg of acrylic rubber: 12°C, $P_{CN}/P_{CO} = 0.001$)
- (C2) SG-P3 solvent-modified product (product obtained by
- 15 modifying the solvent of SG-P3 (trade name, manufactured by Nagase ChemteX Corp., methyl ethyl ketone solution of the acrylic rubber), weight average molecular weight of acrylic rubber: 800000, theoretical Tg of acrylic rubber: 12°C, $P_{CN}/P_{CO} = 0.070$)
- [0103] (Measurement of IR spectrum)
- 20 The P_{CN}/P_{CO} of (C1) and (C2) were calculated according to the following method. First, samples obtained by removing the solvent from (C1) and (C2) were subjected to measurement of transmission IR spectra by the KBr tablet method, so that the absorbance was plotted on the axis of ordinate and the wavenumber (cm^{-1}) was plotted on the axis
- 25 of abscissa. For the measurement of the IR spectra, FT-IR6300 (manufactured by JASCO Corp., light source: high luminance ceramic

light source, detector: DLATGS) was used.

[0104] (Height P_{CO} of absorption peak originating from stretching vibration of carbonyl group)

5 A peak having the highest absorbance between two points at 1670 cm^{-1} and 1860 cm^{-1} was designated as a peak point. A straight line between two points at 1670 cm^{-1} and 1860 cm^{-1} was designated as a baseline, a point having the same wavenumber as the peak point on this baseline was designated as baseline point, and the difference in the absorbance between the baseline point and the peak point was
10 designated as the height (P_{CO}) of an absorption peak originating from stretching vibration of a carbonyl group.

[0105] (Height P_{CN} of peak originating from stretching vibration of nitrile group)

15 In the same IR spectrum as that used to determine the P_{CO} , a peak having the highest absorbance between two points at 2270 cm^{-1} and 2220 cm^{-1} was designated as a peak point. A straight line between two points at 2270 cm^{-1} and 2220 cm^{-1} was designated as a baseline, a point having the same wavenumber as the peak point on this baseline was designated as baseline point, and the difference in the absorbance
20 between the baseline point and the peak point was designated as the height (P_{CN}) of a peak originating from stretching vibration of a nitrile group.

[0106] (D) Heterocyclic compound

- 25 (D1) Benzotriazole
(D2) 5-Aminotetrazole
(D3) 5-Methyltetrazole

(D4) 3-Mercaptotriazole

[0107] (E) Inorganic filler

(E1) SC2050-HLG (trade name, manufactured by Admatechs Co., Ltd., silica filler dispersion liquid, average particle size 0.50 μm)

5 (E2) YA050C-HHG (trade name, manufactured by Admatechs Co., Ltd., silica filler dispersion liquid, average particle size 0.05 μm)

[0108] (F) Coupling agent

(F1) A-189 (trade name, manufactured by Nippon Unicar Company Limited, γ -mercaptopropyltrimethoxysilane)

10 (F2) A-1160 (trade name, manufactured by Nippon Unicar Company Limited, γ -ureidopropyltriethoxysilane)

[0109] (G) Curing accelerator

(G1) 2PZ-CN (trade name, manufactured by SHIKOKU CHEMICALS CORPORATION, 1-cyanoethyl-2-phenylimidazole)

15 [0110] <Production of film-shaped adhesive>

Each of the adhesive varnishes thus produced was filtered through a 100-mesh filter and was subjected to vacuum defoaming. As a base material film, a polyethylene terephthalate (PET) film having a thickness of 38 μm that had been subjected to a mold release treatment was prepared, and the adhesive varnish after vacuum defoaming was applied on the PET film. The applied adhesive varnish was heated and dried in two stages for 5 minutes at 90°C and subsequently for 5 minutes at 130°C, and film-shaped adhesives of Comparative Examples 1-1 and 1-2 and Examples 1-1 and 1-2, and Comparative Examples 2-1 and 2-2 and Examples 2-1 to 2-7 in stage B state were obtained. With regard to the film-shaped adhesive, the thickness was adjusted to 10 μm

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by adjusting the coating amount of the adhesive varnish.

[0111] Table 1

		Comparative Example 1-1	Comparative Example 1-2	Example 1-1	Example 1-2
Component (A)	(A1)	11	11	11	11
Component (B)	(B1)	9	9	9	9
Component (C)	(C1)	-	70	69	69
	(C2)	70	-	-	-
Component (D)	(D1)	-	-	0.5	-
	(D2)	-	-	-	0.5
Component (E)	(E1)	8	8	8	8
	(E2)	-	-	-	-
Component (F)	(F1)	0.4	0.4	0.4	0.4
	(F2)	1.2	1.2	1.2	1.2
Component (G)	(G1)	0.02	0.02	0.02	0.02

[0112] Table 2

		Comp. Exam. 2-1	Comp. Exam. 2-2	Exam. 2-1	Exam. 2-2	Exam. 2-3	Exam. 2-4	Exam. 2-5	Exam. 2-6	Exam. 2-7
Component (A)	(A1)	11	11	11	11	11	11	11	11	11
Component (B)	(B1)	9	9	9	9	9	9	9	9	9
Component (C)	(C1)	-	70	69	69	68	69	69	69	68
	(C2)	70	-	-	-	-	-	-	-	-
	(D1)	-	-	0.5	-	-	-	-	-	-
Component (D)	(D2)	-	-	-	0.5	1	-	-	-	-
	(D3)	-	-	-	-	-	0.5	-	-	-
	(D4)	-	-	-	-	-	-	0.05	0.5	1
Component (E)	(E1)	-	-	-	-	-	-	-	-	-
	(E2)	8	8	8	8	8	8	8	8	8
Component (F)	(F1)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	(F2)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Component (G)	(G1)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

[0113] [Measurement of copper ion permeation time]

<Preparation of liquid A>

2.0 g of anhydrous copper(II) sulfate was dissolved in 1020 g of distilled water, the solution was stirred until copper sulfate completely dissolved, and an aqueous solution of copper sulfate in which the copper ion concentration was a concentration of 500 mg/kg in terms of Cu element was prepared. The aqueous solution of copper sulfate thus obtained was designated as liquid A.

[0114] <Preparation of liquid B>

1.0 g of anhydrous sodium sulfate was dissolved in 1000 g of distilled water, and the solution was stirred until sodium sulfate completely dissolved. To this, 1000 g of N-methyl-2-pyrrolidone (NMP) was further added, and the mixture was stirred. Subsequently, the solution was air-cooled to room temperature, and an aqueous solution of sodium sulfate was obtained. The solution thus obtained was designated as liquid B.

[0115] <Measurement of copper ion permeation time>

Each of the film-shaped adhesives (thickness: 10 μm) of Comparative Example 1-1 and Examples 1-1 and 1-2, and Comparative Example 2-1 and Examples 2-1 to 2-7 produced as described above was cut out into a circular shape having a diameter of about 3 cm. Next, two sheets of silicon packing sheets having a thickness of 1.5 mm, an outer diameter of about 3 cm, and an inner diameter of 1.8 cm were prepared. The film-shaped adhesive cut out into a circular shape was interposed between two sheets of silicon packing sheets, and this was interposed between the flange parts of two glass cells each having a

volume of 50 mL and fixed with a rubber band.

[0116] Next, 50 g of liquid A was poured into one of the glass cells, and 50 g of liquid B was poured into the other glass cell. Mars Carbon (manufactured by STAEDTLER Mars GmbH & Co. KG, ϕ 2 mm/130 mm) as a carbon electrode was inserted into each of the cells. The liquid A side was designated as an anode, the liquid B side was designated as a cathode, and the anode and a direct current power supply (manufactured by A&D Co., Ltd., direct current power supply device AD-9723D) were connected. Furthermore, the cathode and the direct current power supply were connected in series through an ammeter (manufactured by Sanwa Electric Instrument Co., Ltd., Digital multimeter PC-720M). At room temperature, voltage was applied at an applied voltage of 24.0 V, and measurement of the current value was initiated after the application. Measurement was conducted until the current value exceeded 15 μ A, and the time point where the current value reached 10 μ A was designated as the copper ion permeation time. The results are presented in Table 3 and Table 4. In the present evaluation, it can be said that as the permeation time is longer, copper ion permeation is suppressed.

[0117] The film-shaped adhesives of Comparative Example 1-1 and Examples 1-1 and 1-2, and Comparative Example 2-1 and Examples 2-1 to 2-7 in stage B state were further heated and dried for one hour at 170°C, and film-shaped adhesives of Comparative Example 1-1 and Examples 1-1 and 1-2, and Comparative Example 2-1 and Examples 2-1 to 2-7 in stage C state were produced.

[0118] The copper ion permeation time was measured in the same

manner as in the measurement of the copper ion permeation time at the time of using the film-shaped adhesives in stage B state, except that the film-shaped adhesives in stage B state were changed to the film-shaped adhesives in stage C state. Incidentally, in the case of using the film-shaped adhesives in stage C state, measurement was conducted until the current value exceeded 5 μ A, and the time point where the current value reached 1 μ A was designated as the copper ion permeation time. The results are presented in Table 3 and Table 4. In the present evaluation, it can be said that as the permeation time is longer, copper ion permeation is suppressed.

[0119] Table 3

		Comp. Exam. 1-1	Exam. 1-1	Exam. 1-2
Copper ion permeation time (minutes)	Stage B @ 10 μ A	80	300	190
	Stage C @ 1 μ A	100	190	570

[0120] Table 4

		Comp. Exam. 2-1	Exam. 2-1	Exam. 2-2	Exam. 2-3
Copper ion permeation time (minutes)	Stage B @ 10 μ A	130	730	310	330
	Stage C @ 1 μ A	80	280	980	1000
		Exam. 2-4	Exam. 2-5	Exam. 2-6	Exam. 2-7
Copper ion permeation time (minutes)	Stage B @ 10 μ A	470	450	300	230
	Stage C @ 1 μ A	480	850	1040	1180

[0121] [Evaluation of adhesive force]

<Production of semiconductor device>

5 A dicing tape (manufactured by Hitachi Chemical Co., Ltd., thickness 110 μ m) was prepared, the film-shaped adhesives (thickness 10 μ m) of Comparative Example 1-2 and Examples 1-1 and 1-2, and Comparative Example 2-2 and Examples 2-1 to 2-7 thus produced were stuck thereto to produce dicing-die bonding integrated adhesive sheets comprising a dicing tape and a film-shaped adhesive. A
10 semiconductor wafer having a thickness of 400 μ m was laminated on the film-shaped adhesive side of the dicing-die bonding integrated adhesive sheet at a stage temperature of 70°C, and dicing samples were produced.

[0122] Each of the dicing samples thus obtained was cut using a fully
15 automatic dicer DFD-6361 (manufactured by DISCO Corporation). Cutting was performed by a step-cut method of using two sheets of

blades, and dicing blades ZH05-SD3500-N1-xx-DD and ZH05-SD4000-N1-xx-BB (all manufactured by DISCO Corporation) were used. The cutting conditions were set to a speed of blade rotation of 4000 rpm, a cutting speed of 50 mm/sec, and a chip size of 7.5 mm × 7.5 mm. Regarding the cutting, first stage cutting was performed such that about 30 μm of the semiconductor wafer would remain, and subsequently, second stage cutting was performed such that an incision of about 20 μm would be inserted into the dicing tape.

[0123] Subsequently, semiconductor chips obtained by cutting were thermally pressure-bonded onto a solder resist (Taiyo Holdings Co., Ltd., trade name: AUS-308). The pressure bonding conditions were set to a temperature of 120°C, a duration of 1 second, and a pressure of 0.1 MPa. Subsequently, the samples obtained by pressure-bonding were introduced into a dryer and were cured for one hour at 170°C.

The semiconductor chips pressure-bonded to the solder resist were cured, and the die shear strength after curing between the semiconductor chip and the solder resist was measured by suspending and pulling the semiconductor chip using a universal bond tester (manufactured by Nordson Advanced Technology (Japan) K.K., trade name: Series 4000) and was evaluated as the adhesive force. The measurement conditions were set to a stage temperature of 250°C. The results are presented in Table 5 and Table 6.

[0124] Table 5

	Comp. Exam. 1-2	Exam. 1-1	Exam. 1-2
Adhesive force (MPa)	0.2	0.6	0.9

[0125] Table 6

	Comp. Exam. 2-2	Exam. 2-1	Exam. 2-2	Exam. 2-3
Adhesive force (MPa)	0.2	1.1	0.9	1.3
	Exam. 2-4	Exam. 2-5	Exam. 2-6	Exam. 2-7
Adhesive force (MPa)	0.5	0.5	1.0	1.5

[0126] As shown in Table 3 and Table 4, a film-shaped adhesive having an acrylic rubber that satisfied the requirement of Formula (1) exhibited a longer copper ion permeation time as compared to a film-shaped adhesive having an acrylic rubber that did not satisfy the requirement of Formula (1) (comparison of Comparative Example 1-2 and Examples 1-1 and 1-2 with Comparative Example 1-1, and comparison of Comparative Example 2-2 and Examples 2-1 to 2-7 with Comparative Example 2-2). This is speculated to be because when an acrylic rubber having a small quantity of nitrile groups (or including no nitrile group) that has a high complex stability constant with copper ion is used, the force of the film-shaped adhesive to uptake copper ions is weakened. Furthermore, from a comparison between Example 1-1 and Example 2-1 and a comparison between Example 1-2 and Example 2-2, it was found that as the average particle size of the inorganic filler is smaller, the copper ion permeation time tends to become longer.

[0127] As shown in Table 5 and Table 6, film-shaped adhesives containing various heterocyclic compounds exhibited further enhanced adhesive force compared to film-shaped adhesives that did not contain heterocyclic compounds (comparison between Comparative Example

1-2 and Examples 1-1 and 1-2, and comparison between Comparative Example 2-2 and Examples 2-1 to 2-7).

[0128] As described above, it was verified that the film-shaped adhesive of the present invention can have copper ion permeation within the adhesive sufficiently suppressed and has superior adhesive force.

Reference Signs List

[0129] 1: film-shaped adhesive, 2: base material, 3: cover film, 6: tacky adhesive layer, 7: dicing tape, 9, 9a, 9b: semiconductor element, 10: support member, 11: wire, 12: sealing material, 13: terminal, 100, 110, 120, 130: adhesive sheet, 200, 210: semiconductor device.

CLAIMS

1. A film-shaped adhesive for adhering a semiconductor element to a support member for mounting the semiconductor element,
the film-shaped adhesive comprising a heat-curable resin, a curing agent, an acrylic rubber, and a heterocyclic compound,
wherein in the infrared absorption spectrum of the acrylic rubber, when the height of an absorption peak originating from stretching vibration of a carbonyl group is designated as P_{CO} , and the height of a peak originating from stretching vibration of a nitrile group is designated as P_{CN} , P_{CO} and P_{CN} satisfy the condition of the following Formula (1), and
the thickness of the film-shaped adhesive is 50 μm or less:
$$P_{CN}/P_{CO} < 0.070 \quad (1).$$
2. The film-shaped adhesive according to claim 1, wherein the heterocyclic compound is an aromatic compound having three or more nitrogen atoms.
3. The film-shaped adhesive according to claim 1 or 2, wherein the heterocyclic compound is at least one selected from the group consisting of a triazole compound and a tetrazole compound.
4. The film-shaped adhesive according to any one of claims 1 to 3, wherein the content of the heterocyclic compound is 0.01 to 2 parts by mass with respect to 100 parts by mass of the total mass of the heat-curable resin, the curing agent, and the acrylic rubber.
5. The film-shaped adhesive according to any one of claims 1 to 4, wherein the film-shaped adhesive further comprises an inorganic filler, and the average particle size of the inorganic filler is 1 μm or less.

6. An adhesive sheet comprising a base material; and the film-shaped adhesive according to any one of claims 1 to 5 provided on one surface of the base material.
7. The adhesive sheet according to claim 6, wherein the base material is a dicing tape.
8. A semiconductor device comprising a semiconductor element; a support member for mounting the semiconductor element; and an adhesive member provided between the semiconductor element and the support member and adhering the semiconductor element to the support member,
- the adhesive member being a cured product of the film-shaped adhesive according to any one of claims 1 to 5.
9. The semiconductor device according to claim 8, wherein the support member includes a member composed of copper.
10. A method for producing a semiconductor device, the method comprising adhering a semiconductor element to a support member using the film-shaped adhesive according to any one of claims 1 to 5.
11. A method for producing a semiconductor device, the method comprising:
- sticking the film-shaped adhesive of the adhesive sheet according to claim 6 or 7 to a semiconductor wafer;
- cutting the semiconductor wafer having the film-shaped adhesive stuck thereto to produce a plurality of individually divided film-shaped adhesive-attached semiconductor elements; and
- adhering each of the film-shaped adhesive-attached semiconductor elements to a support member.

12. The method for producing a semiconductor device according to claim 11, further comprising heating the film-shaped adhesive-attached semiconductor element adhered to the support member, using a reflow furnace.