

[DESCRIPTION]

[TITLE OF THE INVENTION]

PROTECTIVE FILM-FORMING SHEET

Technical Field

5 [0001]

The present invention relates to a sheet for forming a protective film.

Background Art

[0002]

When a large-scale integrated (LSI) package with multiple pins used in  
10 microprocessor units (MPUs), gate arrays, and the like is mounted on a printed wiring  
board, semiconductor chips with convex-shape electrodes (hereinafter also referred to as  
“bumps”) formed on their connection pad portions have been used in the art. In addition,  
a flip-chip mounting method has been adopted, in which the bumps are faced with and  
brought into contact with the corresponding terminal portions on a substrate to mount the  
15 chip by what is called the "face-down method" and melt-bonded or diffusion-bonded.

[0003]

In recent years, as electronic devices have become smaller, lighter, thinner, and  
more functional, high-density mounting has been required also for built-in electronic  
components. Patent Documents 1 to 3 propose solder materials with a low  $\alpha$ -ray dose to  
20 avoid a problem associated with high-density mounting, that is, a problem of a soft error  
in which an  $\alpha$ -ray enters a memory cell of a semiconductor integrated circuit and this  
rewrites a memory content.

Citation List

Patent Literature

25 [0004]

Patent Document 1: JP 4472752 B

Patent Document 2: JP 2011-214040 A

Patent Document 3: WO 2012/120982

## Summary of Invention

### 5 Technical Problem

[0005]

On the other hand, the increasing demand for high-density mounting of electronic components has also prompted an increasing demand for fine-pitched bumps included in semiconductor chips. However, fine-pitched bumps included in  
10 semiconductor chips creates new problems. For example, in electrically connecting a semiconductor chip and a wiring board via ball bumps, the ball bumps are crushed and spread in the lateral direction, and the ball bumps come into contact with each other and cause a short circuit problem. In addition, to meet the demand for even higher density mounting, three-dimensional high-density mounting, in which semiconductor packages  
15 are stacked in the height direction, is also investigated; in this case, ball bumps are gradually crushed by the weight of the semiconductor packages themselves, and this may lead to a short circuit.

[0006]

With the problems above in mind, the present inventors diligently investigated  
20 and created a sheet for forming a protective film, with which ball bumps are prevented from being crushed and being spread in the lateral direction. In addition, also in a semiconductor chip having pillar bumps, bending of the pillar bumps or the like may bring the pillar bumps into contact with each other, and this may likely cause a short circuit. The sheet created was found to be effective also in solving such a problem in the  
25 pillar bumps.

[0007]

Thus, an object of the present invention is to provide a sheet for forming a protective film, with which a short circuit between fine-pitched bumps can be prevented.

Solution to Problem

5 [0008]

The present inventors have found that the above problems can be solved by the following invention.

That is, the present invention relates to (1) to (9) below.

(1) A sheet for forming a protective film, the sheet having a laminated structure  
10 of a curable resin film (x) and a support sheet (Y), wherein

the sheet for forming a protective film is to be used to form a protective film (X) on a bump-formed surface of a semiconductor wafer, the semiconductor wafer including a plurality of bumps and satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) below:

• Requirement ( $\alpha 1$ ): A width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to  
15 350  $\mu m$ ; and

• Requirement ( $\alpha 2$ ): A pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I) below:

$$[(BM_p)/(BM_w)] \leq 1.0 \quad (I); \text{ and}$$

the sheet for forming a protective film satisfies Requirements ( $\beta 1$ ) to ( $\beta 3$ )  
20 below:

• Requirement ( $\beta 1$ ): A modulus of elasticity in tension at 23°C,  $E'$  (23°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^7$  Pa to  $1 \times 10^{10}$  Pa;

• Requirement (β2): A modulus of elasticity in tension at 260°C, E' (260°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^5$  Pa to  $1 \times 10^8$  Pa; and

5       • Requirement (β3): A thickness ( $X_T$ ) (unit:  $\mu\text{m}$ ) at 23°C of the protective film (X) formed by curing the curable resin film (x) and a height ( $BM_h$ ) (unit:  $\mu\text{m}$ ) of the bump satisfy Relationship (II) below:

$$[(X_T)/(BM_h)] \geq 0.2 \quad (\text{II}).$$

(2) The sheet for forming a protective film according to (1), the sheet further satisfying Requirement (α3a) below:

10       • Requirement (α3a): The height ( $BM_h$ ) of the bump and the width ( $BM_w$ ) of the bump satisfy Relationship (IIIa) below:

$$0.2 \leq [(BM_h)/(BM_w)] \leq 1.0 \quad (\text{IIIa}).$$

(3) The sheet for forming a protective film according to (1), the sheet further satisfying Requirement (α3b) below:

15       • Requirement (α3b): The height ( $BM_h$ ) of the bump and the width ( $BM_w$ ) of the bump satisfy Relationship (IIIb) below:

$$0.5 \leq [(BM_h)/(BM_w)] \leq 5.0 \quad (\text{IIIb}).$$

(4) The sheet for forming a protective film according to any of (1) to (3), the sheet further satisfying Requirement (α4) below:

20       • Requirement (α4): The height ( $BM_h$ ) of the bump is from 15  $\mu\text{m}$  to 300  $\mu\text{m}$ .

(5) The sheet for forming a protective film according to any of (1) to (4), wherein the support sheet (Y) is a back grinding tape.

(6) A method of manufacturing a semiconductor wafer with a protective film, the method including:

(S1) preparing a semiconductor wafer having a bump-formed surface provided with a plurality of bumps;

(S2) bonding the sheet for forming a protective film described in any of (1) to (5) to the bump-formed surface of the semiconductor wafer with pressing the sheet to the bump-formed surface of the semiconductor wafer, using the curable resin film (x) as a bonding surface; and

(S3) curing the curable resin film (x) to form the protective film (X),  
wherein the semiconductor wafer prepared in the step (S1) satisfies

Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) below:

10           • Requirement ( $\alpha 1$ ): The width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to 350  $\mu m$ ; and

              • Requirement ( $\alpha 2$ ): The pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I) below:

$$[(BM_p)/(BM_w)] \leq 1.0 \quad (I).$$

15           (7) A method of manufacturing a semiconductor chip with a protective film, the method including:

(T1) performing the manufacturing method described in (6) to obtain a semiconductor wafer with a protective film; and

20           (T2) dividing the semiconductor wafer with a protective film into individual pieces.

(8) A method of manufacturing a semiconductor package, the method including:

(U1) performing the manufacturing method described in (7) to obtain a semiconductor chip with a protective film; and

25           (U2) electrically connecting a wiring board and the semiconductor chip with a protective film via the bumps.

(9) The method of manufacturing a semiconductor package according to (8), the method further including:

(U3) filling an underfill material between the wiring board and the semiconductor chip with a protective film.

## 5 Advantageous Effects of Invention

[0009]

An embodiment of the present invention can provide the sheet for forming a protective film, the sheet capable of preventing a short circuit between fine-pitched bumps.

## 10 Brief Description of Drawings

[0010]

Fig. 1 is a schematic cross-sectional view illustrating a configuration of a sheet for forming a protective film.

Fig. 2 is a schematic cross-sectional view illustrating an example of a configuration of a sheet for forming a protective film according to an aspect of the present invention.

Fig. 3 is a schematic cross-sectional view illustrating another example of a configuration of a sheet for forming a protective film according to an aspect of the present invention.

Fig. 4 is a schematic cross-sectional view illustrating yet another example of a configuration of a sheet for forming a protective film according to an aspect of the present invention.

Fig. 5 is a schematic cross-sectional view illustrating an example of a semiconductor wafer having a plurality of bumps.

Fig. 6 is a schematic cross-sectional view illustrating another example of a semiconductor wafer having a plurality of bumps.

Fig. 7 is an enlarged top view of three bumps on a semiconductor wafer to illustrate the definition of a pitch ( $BM_P$ ) of the bumps and a width ( $BM_w$ ) of the bump.

5 Fig. 8 is a schematic cross-sectional view illustrating step (S2) of a method of manufacturing a semiconductor wafer with a protective film according to an aspect of the present invention.

Fig. 9 is a schematic cross-sectional view illustrating step (S3) of a method of manufacturing a semiconductor wafer with a protective film according to an aspect of the present invention.

Fig. 10 is a schematic cross-sectional view illustrating step (U2) of a method of manufacturing a semiconductor package according to an aspect of the present invention.

Fig. 11 is a schematic cross-sectional view illustrating a relationship between a height ( $BM_h$ ) (unit:  $\mu m$ ) of a bump and a thickness ( $X_T$ ) (unit:  $\mu m$ ) at 23°C of a protective film (X) formed by curing a curable resin film (x).

#### Description of Embodiments

[0011]

In the present specification, “active components” refer to components excluding a diluent solvent, such as water or an alcohol, from components contained in a target composition.

In addition, in the present specification, “(meth)acrylic acid” refers to both “acrylic acid” and “methacrylic acid”, and the same is true of other similar terms.

Furthermore, in the present specification, “weight average molecular weight” is a polystyrene equivalent value measured by a gel permeation chromatography (GPC) method.

Moreover, in the present specification, the lower and upper limits of a preferred numerical range (e.g., a range of content) described in series can each be independently combined. For example, from the description “preferably from 10 to 90, more preferably from 30 to 60”, the “preferred lower limit (10)” and the “preferred upper limit (60)” can  
5 be combined as “from 10 to 60”.

[0012]

#### Aspects of sheet for forming protective film

A sheet for forming a protective film according to an embodiment of the present invention has a layered structure of a curable resin film (x) and a support sheet (Y).

10 The sheet for forming a protective film according to an embodiment of the present invention is to be used to form a protective film (X) on a bump-formed surface of a semiconductor wafer, the semiconductor wafer including a plurality of bumps and satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) below:

- Requirement ( $\alpha 1$ ): A width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to  
15 350  $\mu m$ ; and

- Requirement ( $\alpha 2$ ): A pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I) below:

$$[(BM_p)/(BM_w)] \leq 1.0 \quad (I).$$

In addition, the sheet for forming a protective film according to an embodiment  
20 of the present invention satisfies Requirements ( $\beta 1$ ) to ( $\beta 3$ ) below:

- Requirement ( $\beta 1$ ): A modulus of elasticity in tension at 23°C,  $E'$  (23°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^7$  Pa to  $1 \times 10^{10}$  Pa;

• Requirement (β2): A modulus of elasticity in tension at 260°C, E' (260°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^5$  Pa to  $1 \times 10^8$  Pa; and

• Requirement (β3): A thickness ( $X_T$ ) (unit: μm) at 23°C of the protective film (X) formed by curing the curable resin film (x) and a height ( $BM_h$ ) (unit: μm) of the bump satisfy Relationship (II) below:

$$[(X_T)/(BM_h)] \geq 0.2 \quad (II).$$

[0013]

That is, the sheet for forming a protective film according to an embodiment of the present invention is used on a bump-formed surface of a semiconductor wafer, the semiconductor having fine-pitched bumps and satisfying Requirements (α1) and (α2) above. In addition, the sheet for forming a protective film according to an embodiment of the present invention has a layered structure of the curable resin film (x) and the support sheet (Y) as a specific configuration and satisfies Requirements (β1) to (β3) above related to the curable resin film (x).

[0014]

The present inventors have formed the protective film (X) on a bump-formed surface of a semiconductor wafer having fine-pitched bumps and satisfying Requirements (α1) and (α2) above using the sheet for forming a protective film having a laminated structure of the curable resin film (x) and the support sheet (Y) and satisfying Requirements (β1) to (β3) above related to the curable resin film (x) and have found that this can prevent crushing and deformation of the bumps and a short circuit between fine-pitched bumps.

Hereinafter, Requirements ( $\beta 1$ ) to ( $\beta 3$ ) above related to the protective film (X) specified in the sheet for forming a protective film according to an embodiment of the present invention will be described.

[0015]

5 Requirement ( $\beta 1$ )

Requirement ( $\beta 1$ ) specifies that a modulus of elasticity in tension at 23°C,  $E'$  (23°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^7$  Pa to  $1 \times 10^{10}$  Pa.

With the modulus of elasticity,  $E'$  (23°C), lower than  $1 \times 10^7$  Pa, the protective  
10 film (X) may fail to prevent crushing and deformation of the bumps, and allow the bumps to come into contact with each other resulting in short-circuit.

On the other hand, with the modulus of elasticity,  $E'$  (23°C), higher than  $1 \times 10^{10}$  Pa, stress during heating and cooling would increase, and this would impose a load to the bumps and reduce the reliability.

15 Here, from the viewpoint of further facilitating the prevention of crushing and deformation of the bumps as well as reducing a load to the bumps during heating and cooling, the modulus of elasticity in tension at 23°C,  $E'$  (23°C), of the protective film (X) formed by curing the curable resin film (x) is preferably from  $3 \times 10^7$  Pa to  $8 \times 10^9$  Pa, more preferably from  $5 \times 10^7$  Pa to  $7 \times 10^9$  Pa, and even more preferably from  $7 \times 10^7$  Pa  
20 to  $6 \times 10^9$  Pa.

The protective film (X) with the modulus of elasticity in tension,  $E'$  (23°C), specified in Requirement ( $\beta 1$ ) is formed by curing the curable resin film (x). The method of preparing the curable resin film (x) for forming the protective film (X) will be described later.

25 [0016]

Requirement ( $\beta 2$ )

Requirement ( $\beta 2$ ) specifies that a modulus of elasticity in tension at 260°C,  $E'$  (260°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^5$  Pa to  $1 \times 10^8$  Pa.

5           With the modulus of elasticity,  $E'$  (260°C), lower than  $1 \times 10^5$  Pa, the protective film (X) may fail to prevent crushing and deformation of the bumps especially in a heating temperature range (e.g., from 250°C to 270°C) in electrically bonding a wiring board and a semiconductor wafer having the bumps via the bumps, and allow the bumps to come into contact with each other, resulting in short-circuit.

10           On the other hand, with the modulus of elasticity,  $E'$  (260°C), higher than  $1 \times 10^8$  Pa, stress during heating and cooling would increase, and this would impose a load to the bumps and reduce the reliability and bondability.

          Here, from the viewpoint of further facilitating the prevention of crushing and deformation of the bumps as well as reducing a load to the bumps during heating and cooling, the modulus of elasticity in tension at 260°C,  $E'$  (260°C), of the protective film (X) formed by curing the curable resin film (x) is preferably from  $7 \times 10^5$  Pa to  $3 \times 10^7$  Pa, more preferably from  $9 \times 10^5$  Pa to  $2 \times 10^7$  Pa, and even more preferably from  $1 \times 10^6$  Pa to  $1.5 \times 10^7$  Pa.

20           The protective film (X) with the modulus of elasticity in tension,  $E'$  (260°C), specified in Requirement ( $\beta 2$ ) is formed by curing the curable resin film (x). The method of preparing the curable resin film (x) for forming the protective film (X) will be described later.

[0017]

Requirement ( $\beta 3$ )

Requirement (β3) specifies a relationship between the thickness ( $X_T$ ) (unit:  $\mu\text{m}$ ) at 23°C of the protective film (X) formed by curing the curable resin film (x) and the height ( $BM_h$ ) (unit:  $\mu\text{m}$ ) of the bump. Specifically, the relationship satisfies Relationship (II) below:

5 
$$[(X_T)/(BM_h)] \geq 0.2 \quad (\text{II}).$$

With  $[(X_T)/(BM_h)] < 0.2$ , the covering height of the protective film (X) to the height ( $BM_h$ ) of the bump would be insufficient, the protective film (X) may fail to prevent crushing and deformation of the bumps, and allow the bumps to come into contact with each other resulting in short-circuit.

10 The upper limit of  $[(X_T)/(BM_h)]$  is not particularly limited but is preferably 1.0 or less and more preferably less than 1.0 from the viewpoint of exposing the bump top from the protective film (X).

Here, from the viewpoints of further facilitating the prevention of crushing and deformation of the bumps and exposing the bump top from the protective film (X), the relationship preferably satisfies Relationship (IIa) below in Requirement (β3):

[0018]

$$P \leq [(X_T)/(BM_h)] \leq Q \quad (\text{IIa})$$

where in Relationship (IIa), P is 0.2, preferably 0.30, more preferably 0.40, and even more preferably 0.50; and

20 in addition, in Relationship (IIa), Q is preferably 1.0, more preferably 0.90, and even more preferably 0.80.

[0019]

The thickness of the curable resin film (x) satisfying the relationship specified by Requirement (β3) can be adjusted based on a relationship between the thickness of the curable resin film (x) and the thickness of the protective film (X) formed by curing the

25

curable resin film (x), and information, such as the height of the bump included in the semiconductor wafer to be used.

A relationship between the height ( $BM_h$ ) (unit:  $\mu\text{m}$ ) of the bump and the thickness ( $X_T$ ) (unit:  $\mu\text{m}$ ) at 23°C of the protective film (X) formed by curing the curable resin film (x) is illustrated in Fig. 11.

The thickness ( $X_T$ ) (unit:  $\mu\text{m}$ ) at 23°C of the protective film (X) formed by curing the curable resin film (x) means, in paying attention to a bump (bump BM) whose height ( $BM_h$ ) is measured as illustrated in Fig. 11, the height of a position 50 from a bump-formed surface 41a, the position farthest from the bump-formed surface 41a in the contact part between the bump and the protective film (X).

It should be noted that the position 50 farthest from the bump-formed surface 41a is determined in the region where the protective film (X) formed on the bump-formed surface 41a is continuously present. Thus, for example, for determination of the position 50 farthest from the bump-formed surface 41a, a contact part between the bump and the protective film (X) is excluded, the protective film (X) being partially present at the bump top and to be removed by exposure treatment (plasma etching treatment) described later. In addition, when the exposure treatment (plasma etching treatment) described later is performed, the thickness after retraction of the protective film (X) by the exposure treatment needs to satisfy Relationship (II) above (0.2  $\mu\text{m}$  or greater). That is, regardless of the presence or absence of the exposure treatment described later, the thickness of the protective film (X), of course, needs to satisfy Relationship (II) above (0.2  $\mu\text{m}$  or greater) immediately before electrically connecting the semiconductor chip and the wiring board via the ball bumps.

The height ( $BM_h$ ) of the bump and the thickness ( $X_T$ ) of the protective film (X) can be measured, for example, by cutting the semiconductor wafer with the protective

film (X) in the direction perpendicular to the bump-formed surface and passing through the center of the bump, and observing the cross-section after cutting with an optical microscope.

[0020]

5 Hereinafter, the sheet for forming a protective film according to an embodiment of the present invention will be described in detail also with a method of preparing the curable resin film (x) for forming the protective film (X) satisfying Requirement ( $\beta$ 1) and Requirement ( $\beta$ 2) in mind.

[0021]

10 Configuration of sheet for forming a protective film

A configuration example of the sheet for forming a protective film according to an embodiment of the present invention is illustrated in Fig. 1.

The sheet for forming a protective film according to an aspect of the present invention is provided with the curable resin film (x) on one surface of the support sheet (Y) as in a sheet 1 for forming a protective film illustrated in Fig. 1. The curable resin film (x) is provided on one side of the support sheet (Y) and thus the curable resin film (x) is stably supported and protected when the curable resin film (x) is transported as a product package or when the curable resin film (x) is conveyed in the process.

[0022]

20 In addition, configuration examples of the sheet for forming a protective film according to an aspect of the present invention are illustrated in Figs. 2 to 4.

In the sheet for forming a protective film according to an aspect of the present invention, as in a sheet 1a for forming a protective film illustrated in Fig. 2, the support sheet (Y) is a substrate 11, and the curable resin film (x) is provided on one surface of the substrate 11.

25

Furthermore, in the sheet for forming a protective film according to an aspect of the present invention, as in a sheet 1b for forming a protective film illustrated in Fig. 3, the support sheet (Y) is a pressure sensitive adhesive (PSA) sheet in which a substrate 11 and a PSA layer 21 are laminated, and the PSA layer 21 of the PSA sheet and the curable resin film (x) may be laminated by bonding.

Moreover, in the sheet for forming a protective film according to an aspect of the present invention, as in a sheet 1c for forming a protective film illustrated in Fig. 4, the support sheet (Y) is a PSA sheet in which a substrate 11, an intermediate layer 31, and a PSA layer 21 are laminated in this order, and the PSA layer 21 of the PSA sheet and the curable resin film (x) may be laminated by bonding. The PSA sheet in which the substrate 11, the intermediate layer 31, and the PSA layer 21 are laminated in this order can be suitably used as a back grinding tape. That is, the sheet 1c for forming a protective film illustrated in Fig. 4 has a back grinding tape serving as the support sheet (Y) and thus can be suitably used when the curable resin film (x) of the sheet 1c for forming a protective film and the bump-formed surface of the semiconductor wafer having a plurality of bumps are laminated by bonding, and then a surface of the semiconductor wafer, the surface (hereinafter also referred to as a “back surface of the semiconductor wafer”) opposite from the bump-formed surface of the semiconductor wafer, is ground to reduce the thickness of the semiconductor wafer.

[0023]

Hereinafter, the curable resin film (x) and the support sheet (Y) used in the sheet for forming a protective film according to an embodiment of the present invention will be described.

[0024]

Curable resin film (x)

The curable resin film (x) is a film for protecting a bump-formed surface of a semiconductor wafer having a plurality of bumps and forms the protective film (X) by curing by heating or energy ray irradiation. That is, the curable resin film (x) may be a thermosetting resin film (x1), which is cured by heating, or may be an energy ray-curable resin film (x2), which is cured by energy ray irradiation.

In the present specification, the “energy ray” means an electromagnetic wave or a charged particle beam having an energy quantum. Examples of the energy ray include ultraviolet light and electron beams and preferably include ultraviolet light.

[0025]

The physical properties of the curable resin film (x) can be adjusted by adjusting either a type or an amount of, or both a type and an amount of a component contained in the curable resin film (x).

[0026]

Hereinafter, the thermosetting resin film (x1) and the energy ray-curable resin film (x2) will be described.

[0027]

Thermosetting resin film (x1)

The thermosetting resin film (x1) contains a polymer component (A) and a thermosetting component (B).

The thermosetting resin film (x1) is formed, for example, from a thermosetting resin composition (x1-1) containing the polymer component (A) and the thermosetting component (B).

The polymer component (A) is a component that can be regarded as being formed by a polymerization reaction of a polymerizable compound. The thermosetting component (B) is a component that can undergo a curing (polymerization) reaction with

heat as a trigger for the reaction. The curing (polymerization) reaction also includes a polycondensation reaction.

In the following description of the present specification, “the content of each component in the total amount of the active components of the thermosetting resin composition (x1-1)” is synonymous with “the content of each component of the thermosetting resin film (x1) formed from the thermosetting resin composition (x1-1)”.

[0028]

Polymer component (A)

The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) contain the polymer component (A).

The polymer component (A) is a polymer compound for imparting film formability and flexibility to the thermosetting resin film (x1). One polymer component (A) may be used alone or two or more in combination. When two or more polymer components (A) are used in combination, their combination and ratios can be freely selected.

[0029]

Examples of the polymer component (A) include poly(vinyl acetal)s, acrylic resins (resins having a (meth)acryloyl group), polyesters, urethane-based resins (resins having a urethane bond), acrylic urethane resins, silicone-based resins (resins having a siloxane bond), rubber-based resins (resins having a rubber structure), phenoxy resins, and thermosetting polyimides. One of these can be used alone or two or more in combination.

Among these, one or more type(s) selected from poly(vinyl acetal)s and acrylic resins are preferred.

Hereinafter, poly(vinyl acetal)s and acrylic resins, which are preferred as the polymer component (A), will be described as examples.

[0030]

• Poly(vinyl acetal)

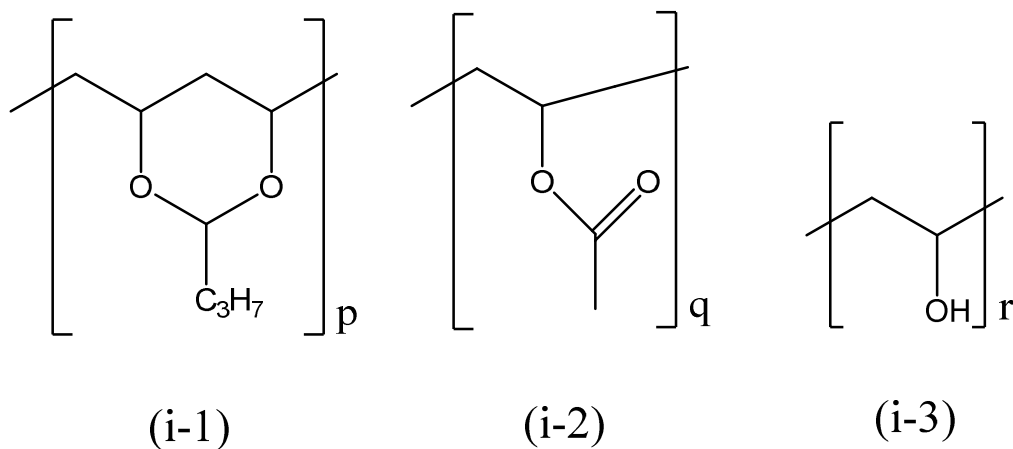
5           The poly(vinyl acetal) used as the polymer component (A) is not particularly limited, and for example, a known poly(vinyl acetal) can be used.

Here, among the poly(vinyl acetal)s, examples include poly(vinyl formal)s and poly(vinyl butyral)s, and a poly(vinyl butyral) is more preferred.

10           The poly(vinyl butyral) is preferably a poly(vinyl butyral) having constitutional units represented by Formulas (i-1), (i-2), and (i-3) from the viewpoint of adhesion improvement between the bump-formed surface of the semiconductor wafer and the protective film (X).

[0031]

[Chem. 1]



15

In Formulas (i-1), (i-2), and (i-3) above, p, q, and r are content ratios (mol%) of the respective constitutional units.

[0032]

The weight average molecular weight ( $M_w$ ) of the poly(vinyl acetal) is preferably from 5000 to 200000, more preferably from 8000 to 100000, even more preferably from 9000 to 80000, and still more preferably from 10000 to 50000. The weight average molecular weight of the poly(vinyl acetal) is in such a range, and this  
5 facilitates improving the adhesion between the bump-formed surface of the semiconductor wafer and the protective film (X). In addition, this increases an effect of reducing the protective film (X) remaining at the upper portion of the bump (the top of the bump and the region near the top).

[0033]

10 The content ratio  $p$  (a degree of butyralization) of the constitutional unit having a butyral group represented by Formula (i-1) above is preferably from 40 to 90 mol%, more preferably from 50 to 85 mol%, and even more preferably from 60 to 76 mol% based on all constitutional units of the polymer component (A).

[0034]

15 The content ratio  $q$  of the constitutional unit having an acetyl group represented by Formula (i-2) above is preferably from 0.1 to 9 mol%, more preferably from 0.5 to 8 mol%, and even more preferably from 1 to 7 mol% based on all constitutional units of the polymer component (A).

[0035]

20 The content ratio  $r$  of the constitutional unit having a hydroxyl group represented by Formula (i-3) above is preferably from 10 to 60 mol%, more preferably from 10 to 50 mol%, and even more preferably from 20 to 40 mol% based on all constitutional units of the polymer component (A).

[0036]

A glass transition temperature ( $T_g$ ) of the poly(vinyl acetal) is preferably from 40 to 80°C and more preferably from 50 to 70°C. The  $T_g$  of the poly(vinyl acetal) is in such a range, and this increases an effect of reducing the protective film (X) remaining at the upper portion of the bump when the thermosetting resin film (x1) is bonded to the  
5 bump-formed surface of the wafer with bumps and also can sufficiently harden the protective film formed by thermally curing the thermosetting resin.

In the present specification, the glass transition temperature ( $T_g$ ) of the polymer (resin) is a value measured by a method described Examples below.

[0037]

10 The content ratio of the three types of constitutional units constituting the poly(vinyl butyral) may be freely adjusted according to the desired physical properties.

In addition, the poly(vinyl butyral) may have a constitutional unit other than the three types of constitutional units, but the content of the three types of constitutional units is preferably from 80 to 100 mol%, more preferably from 90 to 100 mol%, and  
15 even more preferably 100 mol% based on the total amount of the poly(vinyl butyral).

[0038]

- Acrylic resin

Examples of the acrylic resin include known acrylic resins.

A weight average molecular weight ( $M_w$ ) of the acrylic resin is preferably from  
20 10000 to 2000000 and more preferably from 100000 to 1500000.

The weight average molecular weight of the acrylic resin is not less than the lower limit described above, and this facilitates improving shape stability (stability over time during storage) of the thermosetting resin film (x1). In addition, the weight average molecular weight of the acrylic resin is not greater than the upper limit described above,  
25 and this allows the thermosetting resin film (x1) to easily conform to an uneven surface

of an adherend, and for example, this easily prevents the occurrence of a void or the like between the adherend and the thermosetting resin film (x1).

[0039]

A glass transition temperature (T<sub>g</sub>) of the acrylic resin is preferably from -60 to 5 70°C and more preferably from -30 to 50°C.

The glass transition temperature (T<sub>g</sub>) of the acrylic resin is not lower than the lower limit described above, and this reduces the adhesive strength between the protective film (X) and the support sheet (Y) and improves the peelability of the support sheet (Y). In addition, the glass transition temperature (T<sub>g</sub>) of the acrylic resin is not 10 higher than the upper limit described above, and this improves the adhesive strength between the thermosetting resin film (x1) and the protective film (X).

[0040]

Examples of the acrylic resin include polymers of one or two or more type(s) of (meth)acrylic esters; and copolymers of two or more types of monomers selected from 15 (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, N-methylolacrylamide, and the like.

[0041]

Examples of the (meth)acrylic ester constituting the acrylic resin include:

alkyl (meth)acrylates in which the alkyl group constituting the allyl ester has a 20 chain structure having from 1 to 18 carbons, such as methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, sec-butyl(meth)acrylate, tert-butyl(meth)acrylate, pentyl(meth)acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, isooctyl(meth)acrylate, n-octyl(meth)acrylate, n- 25 nonyl(meth)acrylate, isononyl(meth)acrylate, decyl(meth)acrylate,

undecyl(meth)acrylate, dodecyl(meth)acrylate (lauryl(meth)acrylate),  
tridecyl(meth)acrylate, tetradecyl(meth)acrylate (myristyl(meth)acrylate),  
pentadecyl(meth)acrylate, hexadecyl(meth)acrylate (palmityl(meth)acrylate),  
heptadecyl(meth)acrylate, and octadecyl(meth)acrylate (stearyl(meth)acrylate);

5           cycloalkyl(meth)acrylates, such as isobornyl(meth)acrylate and  
dicyclopentanyl(meth)acrylate;

          aralkyl(meth)acrylates, such as benzyl(meth)acrylate;

          cycloalkenyl(meth)acrylates, such as dicyclopentenyl(meth)acrylate;

          cycloalkenyloxyalkyl(meth)acrylates, such as

10       dicyclopentenylloxyethyl(meth)acrylate;

          (meth)acrylate imide;

          glycidyl group-containing (meth)acrylates, such as glycidyl(meth)acrylate;

          hydroxyl group-containing (meth)acrylates, such as

          hydroxymethyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 2-

15       hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2-

          hydroxybutyl(meth)acrylate, 3-hydroxybutyl(meth)acrylate, and 4-

          hydroxybutyl(meth)acrylate; and

          substituted amino group-containing (meth)acrylates, such as N-  
methylaminoethyl(meth)acrylate.

20           In the present specification, the “substituted amino group” means a group in  
which one or two hydrogen atoms of the amino group are replaced by a group(s) other  
than a hydrogen atom(s).

[0042]

          The acrylic resin may be a resin formed by copolymerization of one or more  
25       types of monomers selected from, for example, (meth)acrylic acid, itaconic acid, vinyl

acetate, acrylonitrile, styrene and N-methylolacrylamide in addition to (meth)acrylic esters.

[0043]

One type of monomer alone or two or more types of monomers may constitute  
5 the acrylic resin. When two or more types of monomers constitute the acrylic resin , their combination and ratios can be freely selected.

[0044]

The acrylic resin may have a functional group, such as a vinyl group, a  
(meth)acryloyl group, an amino group, a hydroxyl group, a carboxy group, and an  
10 isocyanate group, that can be attached to another compound.

The functional group of the acrylic resin may be attached to another compound  
via a crosslinking agent (F) described later or may be directly attached to another  
compound without the crosslinking agent (F). The acrylic resin is attached to another  
compound by the functional group, and this tends to improve the reliability of a package  
15 produced using the thermosetting resin film (x1).

[0045]

- Another resin

Here, in an aspect of the present invention, a thermoplastic resin (which may be  
hereinafter abbreviated simply as a “thermoplastic resin”) other than the poly(vinyl  
20 acetal) and the acrylic resin may be used alone as the polymer component (A) without using the acrylic resin or may be used in combination with the poly(vinyl acetal) and/or the acrylic resin .

Using the thermoplastic resin may improve the peelability of the protective film  
(X) from the support sheet (Y), allow the thermosetting resin film (x1) to easily conform

to an uneven surface of an adherend, and thus further prevent the occurrence of a void or the like between the adherend and the thermosetting resin film (x1).

[0046]

A weight average molecular weight of the thermoplastic resin is preferably from  
5 1000 to 100000 and more preferably from 3000 to 80000.

[0047]

A glass transition temperature (T<sub>g</sub>) of the thermoplastic resin is preferably from -30 to 150°C and more preferably from -20 to 120°C.

[0048]

10 Examples of the thermoplastic resin include polyesters, polyurethanes, phenoxy resins, polybutenes, polybutadienes, and polystyrenes.

[0049]

One thermoplastic resin may be used alone or two or more in combination.  
When two or more thermoplastic resins are used, their combination and ratios can be  
15 freely selected.

[0050]

- Content of polymer component (A)

A content of the polymer component (A) is, from the viewpoint of facilitating obtaining the protective film (X) satisfying Requirement (β1) and Requirement (β2),  
20 preferably from 5 to 85 mass%, more preferably from 10 to 80 mass%, even more preferably from 15 to 70 mass%, still more preferably from 15 to 60 mass%, and yet even more preferably from 15 to 50 mass% based on the total amount of the active components of the thermosetting resin composition (x1-1).

[0051]

25 • Aspects of preferred polymer component (A)

As described above, the polymer component (A) is preferably one or more selected from poly(vinyl acetal)s and acrylic resins but is preferably a poly(vinyl acetal) from the viewpoint of facilitating production of the protective film (X) satisfying Requirement (β1) and Requirement (β2).

5           The polymer component (A) may also correspond to the thermosetting component (B). In an embodiment of the present invention, when the thermosetting resin composition (x1-1) contains such a component corresponding to both the polymer component (A) and the thermosetting component (B), the thermosetting resin composition (x1-1) is regarded as containing both the polymer component (A) and the  
10 thermosetting component (B).

[0052]

Thermosetting component (B)

The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) contain the thermosetting component (B).

15           The thermosetting component (B) is a component for curing the thermosetting resin film (x1) to form a hard protective film (X).

One thermosetting component (B) may be used alone or two or more in combination. When two or more thermosetting components (B) are used, their combination and ratios can be freely selected.

20 [0053]

Examples of the thermosetting component (B) include epoxy-based thermosetting resins, thermosetting polyimides, polyurethanes, unsaturated polyesters, and silicone resins. Among these, an epoxy-based thermosetting resin is preferred.

[0054]

The epoxy-based thermosetting resin is composed of an epoxy resin (B1) and a thermal curing agent (B2).

One epoxy-based thermosetting resin may be used alone or two or more in combination. When two or more epoxy-based thermosetting resins are used, their combination and ratios can be freely selected.

[0055]

- Epoxy resin (B1)

Examples of the epoxy resin (B1) include known epoxy resins, for example, including multifunctional epoxy resins, biphenyl compounds, bisphenol A diglycidyl ethers and their hydrogenated products, ortho-cresol novolak epoxy resins, dicyclopentadiene-type epoxy resins, biphenyl-type epoxy resins, bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, phenylene backbone-type epoxy resins, and bifunctional or higher functional epoxy compounds.

[0056]

An epoxy resin having an unsaturated hydrocarbon group may be used as the epoxy resin (B1). The epoxy resin having an unsaturated hydrocarbon group has higher compatibility with the acrylic resin than an epoxy resin having no unsaturated hydrocarbon group. Thus, using the epoxy resin having an unsaturated hydrocarbon group improves the reliability of a package produced using the thermosetting resin film

(x1).

[0057]

Examples of the epoxy resin having an unsaturated hydrocarbon group include compounds in which one or some epoxy group(s) of a multifunctional epoxy resin are converted to a group(s) having an unsaturated hydrocarbon group. Such a compound is formed, for example, by addition reaction of (meth)acrylic acid or its derivative to an

epoxy group. In addition, examples of the epoxy resin having an unsaturated hydrocarbon group include compounds in which a group having an unsaturated hydrocarbon group is directly attached to an aromatic ring or the like constituting the epoxy resin.

- 5           The unsaturated hydrocarbon group is an unsaturated group with polymerizability, and specific examples include an ethenyl group (vinyl group), a 2-propenyl group (allyl group), a (meth)acryloyl group, and a (meth)acrylamide group. Among these, an acryloyl group is preferred.

[0058]

- 10           A number average molecular weight of the epoxy resin (B1) is not particularly limited but is preferably from 300 to 30000, more preferably from 400 to 10000, and even more preferably from 500 to 3000 from the viewpoint of curing properties of the thermosetting resin film (x1) and the strength and heat resistance of the protective film (X) after curing.

- 15           An epoxy equivalent weight of the epoxy resin (B1) is preferably from 100 to 1000 g/eq and more preferably from 300 to 800 g/eq.

[0059]

- One epoxy resin (B1) may be used alone or two or more in combination. When two or more epoxy resins (B1) are used in combination, their combination and ratios can  
20   be freely selected.

[0060]

- Thermal curing agent (B2)

          The thermal curing agent (B2) functions as a curing agent for the epoxy resin (B1).

Examples of the thermal curing agent (B2) include compounds having two or more functional groups that can react with an epoxy group per molecule. Examples of the functional group include a phenolic hydroxyl group, an alcoholic hydroxyl group, an amino group, a carboxy group, and an anhydride group formed by dehydration of an acid group, and the functional group is preferably a phenolic hydroxyl group, an amino group, or an anhydride group formed by dehydration of an acid group, and more preferably a phenolic hydroxyl group or an amino group.

[0061]

Among the thermal curing agents (B2), examples of a phenol-based curing agent having a phenolic hydroxyl group include multifunctional phenolic resins, biphenol, novolak-type phenolic resins, dicyclopentadiene-based phenolic resins, and aralkyl phenolic resins.

Among the thermal curing agents (B2), examples of an amine-based curing agent having an amino group include a dicyandiamide (which may be hereinafter abbreviated as “DICY”).

[0062]

The thermal curing agent (B2) may have an unsaturated hydrocarbon group.

Examples of the thermal curing agent (B2) having an unsaturated hydrocarbon group include compounds in which one or some hydroxyl groups of a phenolic resin are replaced by a group(s) having an unsaturated hydrocarbon group, or compounds in which a group having an unsaturated hydrocarbon group is directly attached to an aromatic ring of a phenolic resin. The unsaturated hydrocarbon group in the thermal curing agent (B2) is the same as the unsaturated hydrocarbon group in the epoxy resin having an unsaturated hydrocarbon group described above.

[0063]

When a phenol-based curing agent is used as the thermal curing agent (B2), the thermal curing agent (B2) preferably has a high softening point or glass transition temperature from the viewpoint of facilitating improving the peelability of the protective film (X) from the support sheet (Y).

5 [0064]

A number average molecular weight of a resin component, such as, for example, a multifunctional phenolic resin, a novolak-type phenolic resin, a dicyclopentadiene-based phenolic resin, and an aralkyl phenolic resin, among the thermal curing agents (B2) is preferably from 300 to 30000, more preferably from 400 to 10000, and even more preferably from 500 to 3000.

10

A molecular weight of the non-resin component, such as, for example, bisphenol or dicyandiamide, among the thermal curing agents (B2) is not particularly limited but is, for example, preferably from 60 to 500.

[0065]

15

One thermal curing agent (B2) may be used alone or two or more in combination. When two or more thermal curing agents (B2) are used, their combination and ratios can be freely selected.

[0066]

20

In the thermosetting resin composition (x1-1), a content of the thermal curing agent (B2) is preferably from 0.1 to 500 parts by mass and more preferably from 1 to 200 parts by mass per 100 parts by mass of the epoxy resin (B1). The content of the thermal curing agent (B2) is not lower than the lower limit described above, and this further facilitates the curing of the thermosetting resin film (x1). In addition, the content of the thermal curing agent (B2) is not higher than the upper limit described above, and this

reduces the moisture absorption rate of the thermosetting resin film (x1) and further improves the reliability of a package produced using the thermosetting resin film (x1).

[0067]

In the thermosetting resin composition (x1-1), a content of the thermosetting component (B) (total content of the epoxy resin (B1) and the thermal curing agent (B2)) is preferably from 50 to 1000 parts by mass, more preferably from 70 to 800 parts by mass, even more preferably from 80 to 600 parts by mass, still more preferably from 90 to 500 parts by mass, and yet even more preferably from 100 to 400 parts by mass per 100 parts by mass of the content of the polymer component (A). The content of the thermosetting component (B) is in such a range, and this reduces the adhesive strength between the protective film (X) and the support sheet (Y) and improves the peelability of the support sheet (Y). In addition, this facilitates obtaining the protective film (X) satisfying Requirement ( $\beta 1$ ) and Requirement ( $\beta 2$ ). Increasing the amount of the thermosetting component (B) relative to the polymer component (A) tends to increase the modulus of elasticity in tension  $E'$ . On the contrary, reducing the amount of the thermosetting component (B) relative to the polymer component (A) tends to reduce the modulus of elasticity in tension  $E'$ .

[0068]

Curing accelerator (C)

The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain a curing accelerator (C).

The curing accelerator (C) is a component for adjusting the curing rate of the thermosetting resin composition (x1-1).

Examples of a preferred curing accelerator include tertiary amines, such as triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, and

tris(dimethylaminomethyl)phenol; imidazoles (imidazoles in which one or more hydrogen atoms are replaced by groups other than hydrogen atoms), such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, and 2-phenyl-4-methyl-5-hydroxymethylimidazole; organic phosphines (phosphines in which one or more hydrogen atoms are replaced by organic groups), such as tributylphosphine, diphenylphosphine, and triphenylphosphine; and tetraphenylboron salts, such as tetraphenylphosphonium tetraphenylborate and triphenylphosphine tetraphenylborate.

[0069]

10           One curing accelerator (C) may be used alone or two or more in combination. When two or more curing accelerators (C) are used, their combination and ratios can be freely selected.

[0070]

          In the thermosetting resin composition (x1-1), a content of the curing accelerator (C) when the curing accelerator (C) is used is preferably from 0.01 to 10 parts by mass and more preferably from 0.1 to 5 parts by mass per 100 parts by mass of the thermosetting component (B). The content of the curing accelerator (C) is not lower than the lower limit described above, and this facilitates obtaining the effect of using the curing accelerator (C) more remarkably. In addition, the content of the curing accelerator (C) is not higher than the upper limit described above, and for example, this increases an effect of preventing the curing accelerator (C) with high polarity from moving in the thermosetting resin film (x1) to the adhesive interface side with an adherend and segregating there under high temperature and high humidity conditions, thus further improving the reliability of a package produced using the thermosetting resin film (x1).

25   [0071]

## Filler (D)

The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain a filler (D).

5 The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) contain the filler (D), and this facilitates adjusting the thermal expansion coefficient of the protective film (X) produced by curing the curable resin film (x1) to an appropriate range, thus further improving the reliability of a package produced using the thermosetting resin film (x1). In addition, the thermosetting resin film (x1) contains the filler (D), and this also can reduce the moisture absorption rate of the protective film (X)  
10 and improve the heat dissipation.

[0072]

The filler (D) may be either an organic filler or an inorganic filler but is preferably an inorganic filler. Examples of a preferred inorganic filler include powders, such as those of silica, alumina, talc, calcium carbonate, titanium white, red iron oxide,  
15 silicon carbide, or boron nitride; spheronized beads of these inorganic fillers; surface-modified products of these inorganic fillers; single crystal fibers of these inorganic fillers; and glass fibers. Among these, the inorganic filler is preferably silica or alumina.

[0073]

One filler (D) may be used alone or two or more in combination.

20 When two or more fillers (D) are used, their combination and ratios can be freely selected.

[0074]

A content of the filler (D) when the filler (D) is used is preferably from 5 to 80 mass% and more preferably from 7 to 60 mass% based on the total amount of the active  
25 components of the thermosetting resin composition (x1-1). The content of the filler (D) is

in such a range, and this further facilitates the adjustment of the thermal expansion coefficient described above.

[0075]

An average particle size of the filler (D) is preferably from 5 nm to 1000 nm,  
5 more preferably from 5 nm to 500 nm, and even more preferably from 10 nm to 300 nm.

The average particle size described above was determined by measuring the outer diameter of one particle in several places and calculating the average value.

[0076]

Coupling agent (E)

10 The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain a coupling agent (E).

Using a coupling agent having a functional group that can react with an inorganic compound or an organic compound as the coupling agent (E) facilitates improving adhesiveness and adhesion of the thermosetting resin film (x1) to an adherend.

15 In addition, using the coupling agent (E) does not impair the heat resistance of the protective film (X) produced by curing the thermosetting resin film (x1) and facilitates improving the water resistance of the protective film (X).

[0077]

The coupling agent (E) is preferably a compound having a functional group that  
20 can react with a functional group contained in the polymer component (A) and the thermosetting component (B) and more preferably a silane coupling agent. Examples of a preferred silane coupling agent include 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropylmethyldiethoxysilane, 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxymethyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-methacryloyloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-(2-

25

aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propylmethyldiethoxysilane, 3-(phenylamino)propyltrimethoxysilane, 3-anilinopropyltrimethoxysilane, 3-ureidopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane, and imidazole silane.

[0078]

One coupling agent (E) may be used alone or two or more in combination.

When two or more coupling agents (E) are used, their combination and ratios can be freely selected.

[0079]

In the thermosetting resin composition (x1-1), a content of the coupling agent (E) when the coupling agent (E) is used is preferably from 0.03 to 20 parts by mass, more preferably from 0.05 to 10 parts by mass, and even more preferably from 0.1 to 5 parts by mass per 100 parts by mass of the total content of the polymer component (A) and the thermosetting component (B). The content of the coupling agent (E) is not lower than the lower limit described above, and this facilitates obtaining the effects of using the coupling agent (E) more remarkably, including improvement of the dispersibility of the filler (D) into the resin and improvement of the adhesiveness of the thermosetting resin film (x1) to an adherend. In addition, the content of the coupling agent (E) is not higher than the upper limit described above, and this further prevents the generation of outgas.

[0080]

Crosslinking agent (F)

When the polymer component (A) having a functional group, such as a vinyl group, a (meth)acryloyl group, an amino group, a hydroxyl group, a carboxy group, or an

isocyanate group, that can be attached to another compound is used, the thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain a crosslinking agent (F) for attaching the functional group to another compound to crosslink.

The crosslinking using the crosslinking agent (F) can adjust the initial adhesive strength and cohesive strength of the thermosetting resin film (x1).

[0081]

Examples of the crosslinking agent (F) include organic polyvalent isocyanate compounds, organic polyvalent imine compounds, metal chelate-based crosslinking agents (crosslinking agents having a metal chelate structure), and aziridine-based crosslinking agents (crosslinking agents having an aziridiny group).

[0082]

Examples of the organic polyvalent isocyanate compound include aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds, and alicyclic polyvalent isocyanate compounds (hereinafter, these compounds may be abbreviated collectively as “the aromatic polyvalent isocyanate compound or the like”); trimers, isocyanurates, and adducts of the aromatic polyvalent isocyanate compound or the like; and terminal isocyanate urethane prepolymers formed by reacting the aromatic polyvalent isocyanate compound or the like and a polyol compound. The “adduct” means a reaction product of the aromatic polyvalent isocyanate compound, aliphatic polyvalent isocyanate compound, or alicyclic isocyanate compound with a low-molecular active hydrogen-containing compound, such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, or castor oil, and examples include xylylene diisocyanate adduct of trimethylolpropane.

[0083]

Examples of the organic polyvalent isocyanate compound more specifically include 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate; 1,3-xylylene diisocyanate; 1,4-xylylene diisocyanate; diphenylmethane-4,4'-diisocyanate; diphenylmethane-2,4'-diisocyanate; 3-methyldiphenylmethane diisocyanate; hexamethylene diisocyanate; 5 isophorone diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; dicyclohexylmethane-2,4'-diisocyanate; compounds in which any one or two or more type(s) of tolylene diisocyanate, hexamethylene diisocyanate, and xylylene diisocyanate are added to all or some of the hydroxyl groups of a polyol, such as trimethylolpropane; and lysine diisocyanate.

10 [0084]

Examples of the organic polyvalent imine compound imine compound include N,N'-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane-tri- $\beta$ -aziridinyl propionate, tetramethylolmethane-tri- $\beta$ -aziridinyl propionate, and N,N'-toluene-2,4-bis(1-aziridinecarboxamide)triethylenemelamine.

15 [0085]

When the organic polyvalent isocyanate compound is used as the crosslinking agent (F), a hydroxyl group-containing polymer is preferably used as the polymer component (A). When the crosslinking agent (F) has an isocyanate group and the polymer component (A) has a hydroxyl group, a crosslinking structure can be easily 20 introduced into the thermosetting resin film (x1) by reaction of the crosslinking agent (F) and the polymer component (A).

[0086]

One crosslinking agent (F) may be used alone or two or more in combination. When two or more crosslinking agents (F) are used, their combination and ratios can be 25 freely selected.

[0087]

In the thermosetting resin composition (x1-1), a content of the crosslinking agent (F) when the crosslinking agent (F) is used is preferably from 0.01 to 20 parts by mass, more preferably from 0.1 to 10 parts by mass, and even more preferably from 0.5 to 5 parts by mass per 100 parts by mass of the content of the polymer component (A). The content of the crosslinking agent (F) is not lower than the lower limit described above, and this produces the effect of using the crosslinking agent (F) more remarkably. In addition, the content of the crosslinking agent (F) is not higher than the upper limit described above, and this prevents overuse of the crosslinking agent (F).

10 [0088]

Energy ray-curable compound (G)

The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain an energy ray-curable resin (G).

The thermosetting resin film (x1) contains the energy ray-curable resin (G), and thus the properties can be changed by energy ray irradiation.

[0089]

The energy ray-curable resin (G) is formed by polymerizing (curing) an energy ray-curable compound. Examples of the energy ray-curable compound include a compound having at least one polymerizable double bond in the molecule, and an acrylate-based compound having a (meth)acryloyl group is preferred.

[0090]

Examples of the acrylate-based compound include chain aliphatic backbone-containing (meth)acrylates, such as trimethylolpropane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate,

dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate; cycloaliphatic backbone-containing (meth)acrylates, such as dicyclopentanyl di(meth)acrylate; poly(alkylene glycol)(meth)acrylates, such as polyethylene glycol di(meth)acrylate; oligoester (meth)acrylates; urethane (meth)acrylate  
5 oligomers; epoxy-modified (meth)acrylates; polyether (meth)acrylates other than the poly(alkylene glycol)(meth)acrylates; and itaconic acid oligomers.

[0091]

A weight average molecular weight of the energy ray-curable compound is preferably from 100 to 30000 and more preferably from 300 to 10000.

10 [0092]

One energy ray-curable compound used for polymerization may be used alone or two or more in combination. When two or more energy ray-curable compounds are used for polymerization, their combination and ratios can be freely selected.

[0093]

15 A content of the energy ray-curable resin (G) when the energy ray-curable resin (G) is used is preferably from 1 to 95 mass%, more preferably from 5 to 90 mass%, and even more preferably from 10 to 85 mass% based on the total amount of the active components of the thermosetting resin composition (x1-1).

[0094]

20 Photopolymerization initiator (H)

When the thermosetting resin film (x1) and the thermosetting resin composition (x1-1) contain the energy ray-curable resin (G), the thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain a photopolymerization initiator (H) to facilitate efficient polymerization reaction of the energy ray-curable resin (G).

25 [0095]

Examples of the photopolymerization initiator (H) include benzophenone, acetophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, methyl benzoin benzoate, benzoin dimethyl ketal, 2,4-diethylthioxanthone, 1-hydroxycyclohexyl phenyl ketone, benzyldiphenyl sulfide, tetramethylthiuram monosulfide, azobisisobutyronitrile, benzyl, 5 dibenzyl, diacetyl, 1,2-diphenylmethane, 2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and 2-chloroanthraquinone.

[0096]

10 One photopolymerization initiator (H) may be used alone or two or more in combination. When two or more photopolymerization initiators (H) are used, their combination and ratios can be freely selected.

[0097]

In the thermosetting resin composition (x1-1), a content of the photopolymerization initiator (H) is preferably from 0.1 to 20 parts by mass, more preferably from 1 to 10 parts by mass, and even more preferably from 2 to 5 parts by mass per 100 parts by mass of the content of the energy ray-curable resin (G).

[0098]

Versatile additive (I)

20 The thermosetting resin film (x1) and the thermosetting resin composition (x1-1) may contain a versatile additive (I) within a range that does not impair the effects of the present invention. The versatile additive (I) is a known additive and can be freely selected according to the purpose, and not particularly limited.

Examples of a preferred versatile additive (I) include plasticizers, antistatic agents, antioxidants, colorants (dyes and pigments), and gettering agents.

25

[0099]

One versatile additive (I) may be used alone or two or more in combination.

When two or more versatile additives (I) are used, their combination and ratios can be freely selected.

- 5           A content of the versatile additive (I) is not particularly limited and is appropriately selected according to the purpose.

[0100]

Solvent

- 10           The thermosetting resin composition (x1-1) preferably further contains a solvent.

The thermosetting resin composition (x1-1) containing a solvent has good handling properties.

- 15           The solvent is not particularly limited, but preferred examples include hydrocarbons, such as toluene and xylene; alcohols, such as methanol, ethanol, 2-propanol, isobutyl alcohol (2-methylpropan-1-ol), and 1-butanol; esters, such as ethyl acetate; ketones, such as acetone and methyl ethyl ketone; ethers, such as tetrahydrofuran; and amides (compounds having an amide bond), such as dimethylformamide and N-methylpyrrolidone.

- 20           One solvent may be used alone or two or more in combination. When two or more solvents are used, their combination and ratios can be freely selected.

The solvent is preferably methyl ethyl ketone or the like from the viewpoint that components contained in the thermosetting resin composition (x1-1) can be more uniformly mixed.

[0101]

- 25           Method of preparing thermosetting resin composition (x1-1)

The thermosetting resin composition (x1-1) is prepared by blending the components for constituting the composition.

The order in which the components are added when blended is not particularly limited, and two or more components may be added simultaneously. When a solvent is  
5 used, the solvent may be used by mixing with any of the components to be blended other than the solvent to predilute the component to be blended, or the solvent may be used by mixing with these components to be blended without prediluting any of the components to be blended other than the solvent.

The method of mixing the components in blending is not particularly limited  
10 and is appropriately selected from known methods, such as a method of mixing by rotating a stirrer, a stirring blade, or the like; a method of mixing using a mixer; and a method of mixing by applying an ultrasonic wave.

A temperature and time when the components are added and mixed are not particularly limited as long as each blended component is not degraded, and are  
15 appropriately adjusted, but the temperature is preferably from 15 to 30°C.

[0102]

Energy ray-curable resin film (x2)

The energy ray-curable resin film (x2) contains an energy ray-curable component (a).

20 The energy ray-curable resin film (x2) is formed, for example, from an energy ray-curable resin composition (x2-1) containing the energy ray-curable component (a).

The energy ray-curable component (a) is preferably uncured, preferably has pressure sensitive adhesion, and more preferably is uncured and has pressure sensitive adhesion.

In the following description of the present specification, “a content of each component based on the total amount of the active components of the energy ray-curable resin composition (x2-1)” is synonymous with “a content of each component of the energy ray-curable resin film (x2) formed from the energy ray-curable resin composition (x2-1)”.

[0103]

Energy ray-curable component (a)

The energy ray-curable component (a) is a component cured by energy ray irradiation and is also a component for imparting film formability and flexibility to the energy ray-curable resin film (x2).

Examples of the energy ray-curable component (a) include a polymer (a1) with a weight average molecular weight of 80000 to 2000000 having an energy ray-curable group, and a compound (a2) with a molecular weight of 100 to 80000 having an energy ray-curable group. The polymer (a1) may be at least partially crosslinked with a crosslinking agent or may be not crosslinked.

[0104]

Polymer (a1)

Examples of the polymer (a1) with a weight average molecular weight of 80000 to 2000000 having an energy ray-curable group include an acrylic resin (a1-1) formed by polymerization of an acrylic-based polymer (a11) having a functional group that can react with a group contained in another compound and an energy ray-curable compound (a12) having a group that can react with the functional group described above and an energy ray-curable group, such as an energy ray-curable double bond.

[0105]

Examples of the functional group that can react with a group contained in another compound include a hydroxyl group, a carboxy group, an amino group, a substituted amino group (a group in which one or two hydrogen atoms of the amino group are replaced by a group(s) other than a hydrogen atom(s)), and an epoxy group.

5 However, in terms of preventing corrosion of a circuit of a semiconductor wafer, semiconductor chip, or the like, the functional group is preferably a group other than a carboxy group. Among these, the functional group is preferably a hydroxyl group.

[0106]

- Acrylic-based polymer (a11) having functional group

10 Examples of the acrylic-based polymer (a11) having a functional group include a polymer formed by copolymerization of an acrylic-based monomer having a functional group and an acrylic-based monomer having no functional group. The acrylic-based polymer (a11) having a functional group may be a polymer formed by further copolymerization of monomers (non-acrylic-based monomers) other than acrylic-based  
15 monomers in addition to the acrylic-based monomers described above. In addition, the acrylic-based polymer (a11) may be a random copolymer or a block copolymer.

[0107]

Examples of the acrylic-based monomer having a functional group include hydroxyl group-containing monomers, carboxy group-containing monomers, amino  
20 group-containing monomers, and epoxy group-containing monomers.

[0108]

Examples of the hydroxyl group-containing monomer include hydroxyalkyl(meth)acrylates, such as hydroxymethyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, 3-

25 hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, 3-

hydroxybutyl(meth)acrylate, and 4-hydroxybutyl(meth)acrylate; and non-(meth)acrylic-based unsaturated alcohols (unsaturated alcohols having no (meth)acryloyl backbone), such as vinyl alcohol and allyl alcohol.

[0109]

- 5           Examples of the carboxy group-containing monomer include ethylenically unsaturated monocarboxylic acids (monocarboxylic acids having an ethylenically unsaturated bond), such as (meth)acrylic acid and crotonic acid; ethylenically unsaturated dicarboxylic acids (dicarboxylic acids having an ethylenically unsaturated bond), such as fumaric acid, itaconic acid, maleic acid, and citraconic acid; anhydrides of the
- 10 ethylenically unsaturated dicarboxylic acids; and carboxyalkyl(meth)acrylates, such as 2-carboxyethyl methacrylate.

[0110]

- The acrylic-based monomer having a functional group is preferably a hydroxyl group-containing monomer or a carboxy group-containing monomer and more preferably
- 15 a hydroxyl group-containing monomer.

[0111]

- One type of acrylic-based monomer constituting the acrylic-based polymer (a11) may be used alone or two or more types in combination. When two or more types of acrylic-based monomers constitute the acrylic-based polymer (a11), their combination
- 20 and ratios can be freely selected.

[0112]

- Examples of the acrylic-based monomer having no functional group include alkyl (meth)acrylates in which the alkyl group constituting the alkyl ester has a chain structure having from 1 to 18 carbons, such as methyl(meth)acrylate, ethyl(meth)acrylate,
- 25 n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate,

isobutyl(meth)acrylate, sec-butyl(meth)acrylate, tert-butyl(meth)acrylate,  
pentyl(meth)acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate, 2-  
ethylhexyl(meth)acrylate, isooctyl(meth)acrylate, n-octyl(meth)acrylate, n-  
nonyl(meth)acrylate, isononyl(meth)acrylate, decyl(meth)acrylate,  
5 undecyl(meth)acrylate, dodecyl(meth)acrylate (lauryl (meth)acrylate),  
tridecyl(meth)acrylate, tetradecyl(meth)acrylate (myristyl(meth)acrylate),  
pentadecyl(meth)acrylate, hexadecyl(meth)acrylate (palmityl(meth)acrylate),  
heptadecyl(meth)acrylate, and octadecyl(meth)acrylate (stearyl(meth)acrylate).

[0113]

10           Examples of the acrylic-based monomer having no functional group also include  
alkoxyalkyl group-containing (meth)acrylates, such as methoxymethyl(meth)acrylate,  
methoxyethyl(meth)acrylate, ethoxymethyl(meth)acrylate, and  
ethoxyethyl(meth)acrylate; (meth)acrylates having an aromatic group, including  
aryl(meth)acrylates, such as phenyl(meth)acrylate; non-crosslinkable (meth)acrylamides  
15 and their derivatives; and (meth)acrylic esters having a non-crosslinkable tertiary amino  
group, such as N,N-dimethylaminoethyl(meth)acrylate and N,N-  
dimethylaminopropyl(meth)acrylate.

[0114]

One type of acrylic-based monomer having no functional group, the monomer  
20 constituting the acrylic-based polymer (a11), may be used alone or two or more types in  
combination. When two or more types of acrylic-based monomers having no functional  
group constitute the acrylic-based polymer (a11), their combination and ratios can be  
freely selected.

[0115]

Examples of the non-acrylic-based monomer include olefins, such as ethylene and norbornene; vinyl acetate; and styrene.

[0116]

One type of non-acrylic-based monomer constituting the acrylic-based polymer (a11) may be used alone or two or more types in combination. When two or more types of non-acrylic-based monomers constitute the acrylic-based polymer (a11), their combination and ratios can be freely selected.

[0117]

In the acrylic-based polymer (a11), a ratio of an amount (content) of the constitutional unit derived from the acrylic-based monomer having a functional group to the total mass of the constitutional units constituting the acrylic-based polymer (a11) is preferably from 0.1 to 50 mass%, more preferably from 1 to 40 mass%, and even more preferably from 3 to 30 mass%. With the ratio in such a range, a content of the energy ray-curable group in the acrylic resin (a1-1) formed by copolymerization of the acrylic-based polymer (a11) and the energy ray-curable compound (a12) can be easily adjusted such that the degree of curing of the protective film (X) is in a preferred range.

[0118]

One type of acrylic-based polymer (a11) constituting the acrylic resin (a1-1) may be used alone or two or more types in combination. When two or more types of acrylic-based polymers (a11) constitute the acrylic resin (a1-1), their combination and ratios can be freely selected.

[0119]

A content of the acrylic resin (a1-1) is preferably from 1 to 60 mass%, more preferably from 3 to 50 mass%, and even more preferably from 5 to 40 mass% based on

the total amount of the active components of the energy ray-curable resin composition (x2-1).

[0120]

- Energy ray-curable compound (a12)

5           The energy ray-curable compound (a12) preferably has one type or two or more types selected from the group consisting of an isocyanate group, an epoxy group, and a carboxy group as a group that can react with a functional group contained in the acrylic-based polymer (a11) and more preferably has an isocyanate group as the group described above.

10           When the energy ray-curable compound (a12) has, for example, an isocyanate group as the group described above, this isocyanate group readily reacts with a hydroxyl group of the acrylic-based polymer (a11) having this hydroxyl group as the functional group described above.

[0121]

15           The energy ray-curable compound (a12) has preferably from 1 to 5 and more preferably 1 or 2 energy ray-curable groups in one molecule.

[0122]

Examples of the energy ray-curable compound (a12) include 2-methacryloyloxyethyl isocyanate, meta-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate, 20 methacryloyl isocyanate, allyl isocyanate, and 1,1-(bisacryloyloxymethyl)ethyl isocyanate; acryloyl monoisocyanate compounds formed by a reaction of a diisocyanate compound or a polyisocyanate compound with hydroxyethyl(meth)acrylate; and acryloyl monoisocyanate compounds formed by a reaction of a diisocyanate compound or a polyisocyanate compound with a polyol compound, and hydroxyethyl(meth)acrylate.

Among these, the energy ray-curable compound (a12) is preferably 2-methacryloyloxyethyl isocyanate.

[0123]

One energy ray-curable compound (a12) constituting the acrylic resin (a1-1) may be used alone or two or more in combination. When two or more energy ray-curable compounds (a12) constitute the acrylic resin (a1-1), their combination and ratios can be freely selected.

[0124]

In the acrylic resin (a1-1), a ratio of the content of the energy ray-curable group derived from the energy ray-curable compound (a12) to the content of the functional group derived from the acrylic-based polymer (a11) is preferably from 20 to 120 mol%, more preferably from 35 to 100 mol%, and even more preferably from 50 to 100 mol%. The ratio of the content is in such a range, and this further increases the adhesive strength of the protective film (X) after curing. In a case where the energy ray-curable compound (a12) is a monofunctional compound (having one group described above in one molecule), an upper limit of the ratio of the content is 100 mol%, but in a case where the energy ray-curable compound (a12) is a multifunctional compound (having two or more groups described above in one molecule), an upper limit of the ratio of the content may exceed 100 mol%.

[0125]

A weight average molecular weight (Mw) of the polymer (a1) is preferably from 100000 to 2000000 and more preferably from 300000 to 1500000.

[0126]

When the polymer (a1) is at least partially crosslinked with a crosslinking agent, the polymer (a1) may be a polymer in which a monomer not corresponding to any of the

monomers described above as those constituting the acrylic-based polymer (a11) and having a group reacting with the crosslinking agent is polymerized and crosslinked at the group reacting with the crosslinking agent, or may be a polymer in which the monomer is crosslinked at the group derived from the energy ray-curable compound (a12) and  
5 reacting with the functional group described above.

[0127]

One type of polymer (a1) may be used alone or two or more types in combination. When two or more types of polymers (a1) are used, their combination and ratios can be freely selected.

10 [0128]

Compound (a2)

Examples of the energy ray-curable group contained in the compound (a2) with a weight average molecular weight of 100 to 80000 having an energy ray-curable group include a group containing an energy ray-curable double bond, and preferred examples  
15 include a (meth)acryloyl group or a vinyl group.

[0129]

The compound (a2) is not particularly limited as long as the compound satisfies the conditions described above, but examples include low-molecular weight compounds having an energy ray-curable group, an epoxy resin having an energy ray-curable group,  
20 and a phenolic resin having an energy ray-curable group.

[0130]

Among the compounds (a2), examples of the low-molecular weight compound having an energy ray-curable group include multifunctional monomers or oligomers, and an acrylate-based compound having a (meth)acryloyl group is preferred. Examples of the  
25 acrylate-based compound include bifunctional (meth)acrylates, such as 2-hydroxy-3-

(meth)acryloyloxypropyl methacrylate, polyethylene glycol di(meth)acrylate, propoxylated ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryloxypolyethoxy)phenyl]propane, ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryloxy diethoxy)phenyl]propane, 9,9-bis[4-(2-(meth)acryloyloxy ethoxy)phenyl]fluorene, 2,2-bis[4-((meth)acryloxy polypropoxy)phenyl]propane, tricyclodecane dimethanol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, poly(tetramethylene glycol) di(meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 2,2-bis[4-((meth)acryloxyethoxy)phenyl]propane, neopentyl glycol di(meth)acrylate, ethoxylated polypropylene glycol di(meth)acrylate, and 2-hydroxy-1,3-di(meth)acryloxypropane; polyfunctional (meth)acrylates, such as tris(2-(meth)acryloxyethyl)isocyanurate, ε-caprolactone-modified tris(2-(meth)acryloxyethyl)isocyanurate, ethoxylated glycerin tri(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol poly(meth)acrylate, and dipentaerythritol hexa(meth)acrylate; and polyfunctional (meth)acrylate oligomers, such as urethane (meth)acrylate oligomers.

[0131]

Among the compounds (a2), for the epoxy resin having an energy ray-curable group and the phenolic resin having an energy ray-curable group, for example, those described in paragraph [0043] and the like in “JP 2013-194102 A” can be used.

[0132]

A weight average molecular weight (Mw) of the compound (a2) is preferably from 100 to 30000 and more preferably from 300 to 10000.

[0133]

One compound (a2) may be used alone or two or more in combination. When  
5 two or more compounds (a2) are used, their combination and ratios can be freely selected.

[0134]

Polymer (b) having no energy ray-curable group

In a case where the energy ray-curable resin composition (x2-1) and the energy  
10 ray-curable resin film (x2) contain the compound (a2) as the energy ray-curable component (a), the energy ray-curable resin composition (x2-1) and the energy ray-curable resin film (x2) preferably further contain a polymer (b) having no energy ray-curable group as well.

The polymer (b) having no energy ray-curable group may be at least partially  
15 crosslinked with a crosslinking agent or may be not crosslinked.

[0135]

Examples of the polymer (b) having no energy ray-curable group include acrylic-based polymers, phenoxy resins, urethane resins, polyesters, rubber-based resins, and acrylic urethane resins. Among these, the polymer (b) is preferably an acrylic-based  
20 polymer (which may be hereinafter abbreviated as the “acrylic-based polymer (b-1)”).

[0136]

The acrylic-based polymer (b-1) may be a known acrylic-based polymer and for example, may be a homopolymer of one type of acrylic-based monomer or may be a copolymer of two or more types of acrylic-based monomers. In addition, the acrylic-  
25 based polymer (b-1) may be a copolymer of one type or two or more types of acrylic-

based monomers and one type or two or more types of monomers (non-acrylic-based monomers) other than acrylic-based monomers.

[0137]

Examples of the acrylic-based monomer constituting the acrylic-based polymer (b-1) include alkyl(meth)acrylates, (meth)acrylic esters having a cyclic backbone, glycidyl group-containing (meth)acrylic esters, hydroxyl group-containing (meth)acrylic esters, and substituted amino group-containing (meth)acrylic esters.

[0138]

Examples of the alkyl (meth)acrylates include alkyl (meth)acrylates in which the alkyl group constituting the alkyl ester has a chain structure having from 1 to 18 carbons, such as methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, sec-butyl(meth)acrylate, tert-butyl(meth)acrylate, pentyl(meth)acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, isooctyl(meth)acrylate, n-octyl(meth)acrylate, n-nonyl(meth)acrylate, isononyl(meth)acrylate, decyl(meth)acrylate, undecyl(meth)acrylate, dodecyl(meth)acrylate (lauryl(meth)acrylate), tridecyl(meth)acrylate, tetradecyl(meth)acrylate (myristyl(meth)acrylate), pentadecyl(meth)acrylate, hexadecyl(meth)acrylate (palmityl(meth)acrylate), heptadecyl(meth)acrylate, and octadecyl(meth)acrylate (stearyl(meth)acrylate).

[0139]

Examples of the (meth)acrylic ester having a cyclic backbone include cycloalkyl(meth)acrylates, such as isobornyl(meth)acrylate and dicyclopentanylmethacrylate; aralkyl(meth)acrylates, such as benzyl(meth)acrylate; cycloalkenyl(meth)acrylates, such as dicyclopentenyl(meth)acrylate; and cycloalkenyloxyalkyl(meth)acrylates, such as dicyclopentenylmethoxyethyl(meth)acrylate.

[0140]

Examples of the glycidyl group-containing (meth)acrylic ester include glycidyl(meth)acrylate. Examples of the hydroxyl group-containing (meth)acrylate include hydroxymethyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 2-  
5 hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, 3-hydroxybutyl(meth)acrylate, and 4-hydroxybutyl(meth)acrylate.

Examples of the substituted amino group-containing (meth)acrylic ester include N-methylaminoethyl(meth)acrylate.

10 [0141]

Examples of the non-acrylic-based monomer constituting the acrylic-based polymer (b-1) include olefins, such as ethylene and norbornene; vinyl acetate; and styrene.

[0142]

15 Examples of the polymer (b) at least partially crosslinked with a crosslinking agent and having no energy ray-curable group include those in which a reactive functional group in the polymer (b) is reacted with the crosslinking agent.

The reactive functional group is appropriately selected according to the type of crosslinking agent or the like and is not particularly limited. For example, when the  
20 crosslinking agent is a polyisocyanate compound, examples of the reactive functional group include a hydroxyl group, a carboxy group, and an amino group, and among these, a hydroxyl group, which has high reactivity with an isocyanate group, is preferred.

In addition, in a case where the crosslinking agent is an epoxy-based compound, examples of the reactive functional group include a carboxy group, an amino group, and

an amide group, and among these, a carboxy group, which has high reactivity with an epoxy group, is preferred.

However, in terms of preventing corrosion of a circuit of a semiconductor wafer or semiconductor chip, the reactive functional group is preferably a group other than a carboxy group.

[0143]

Examples of the polymer (b) having a reactive functional group and having no energy ray-curable group include those formed by polymerization of a monomer having at least a reactive functional group. In the case of the acrylic-based polymer (b-1), a monomer having a reactive functional group is used as one or both of the acrylic-based monomer and the non-acrylic-based monomer exemplified as the monomer constituting the acrylic-based polymer (b-1). Examples of the polymer (b) having a hydroxyl group as a reactive functional group include those formed, for example, by polymerization of a hydroxyl group-containing (meth)acrylic ester, and in addition to these, examples include those formed by polymerization of a monomer in which one or two or more hydrogen atoms are replaced by the reactive functional group(s) in the acrylic-based monomer or non-acrylic-based monomer previously exemplified.

[0144]

In the polymer (b) having a reactive functional group, a ratio of the amount (content) of the constitutional unit derived from the monomer having a reactive functional group to the total mass of the constitutional units constituting this polymer (b) is preferably from 1 to 20 mass% and more preferably from 2 to 10 mass%. The ratio is in such a range, and this allows the degree of crosslinking to be in a more preferred range in the polymer (b).

[0145]

A weight average molecular weight (Mw) of the polymer (b) having no energy ray-curable group is preferably from 10000 to 2000000 and more preferably from 100000 to 1500000 from the viewpoint of better film formability of the energy ray-curable resin composition (x2-1).

5 [0146]

One type of polymer (b) having no energy ray-curable group may be used alone or two or more types in combination. When two or more types of polymers (b) having no energy ray-curable group are used, their combination and ratios can be freely selected.

[0147]

10 Examples of the energy ray-curable resin composition (x2-1) include those having one or both of the polymer (a1) and compound (a2).

In addition, in a case where the energy ray-curable resin composition (x2-1) contains the compound (a2), the energy ray-curable resin composition (x2-1) preferably further contains the polymer (b) having no energy ray-curable group as well, and in this  
15 case, the energy ray-curable resin composition (x2-1) preferably further contains the polymer (a1) as well.

Furthermore, the energy ray-curable resin composition (x2-1) may contain no compound (a2) and contain both the polymer (a1) and the polymer (b) having no energy ray-curable group.

20 [0148]

In a case where the energy ray-curable resin composition (x2-1) contains the polymer (a1), the compound (a2), and the polymer (b) having no energy ray-curable group, the content of the compound (a2) is preferably from 10 to 400 parts by mass and more preferably from 30 to 350 parts by mass per 100 parts by mass of the total content  
25 of the polymer (a1) and the polymer (b) having no energy ray-curable group.

[0149]

The total content of the energy ray-curable component (a) and the polymer (b) having no energy ray-curable group is preferably from 5 to 90 mass%, more preferably from 10 to 80 mass%, and even more preferably from 20 to 70 mass% based on the total  
5 amount of the active components of the energy ray-curable resin composition (x2-1). The content of the energy ray-curable component is in such a range, and this improves the energy ray-curability of the energy ray-curable resin film (x2).

[0150]

The energy ray-curable resin composition (x2-1) may contain one or two or  
10 more selected from the group consisting of thermosetting components, photopolymerization initiators, fillers, coupling agents, crosslinking agents, and versatile additives according to the purpose in addition to the energy ray-curable component.

For example, using the energy ray-curable resin composition (x2-1) containing an energy ray-curable component and a thermosetting component improves the adhesive  
15 strength of the energy ray-curable resin film (x2) to be formed to an adherend by heating, and this in turn also improves the strength of the protective film (X) formed from this energy ray-curable resin film (x2).

[0151]

Examples of the thermosetting component, photopolymerization initiator, filler,  
20 coupling agent, crosslinking agent, and versatile additive in the energy ray-curable resin composition (x2-1) include the same as those for the thermosetting component (B), photopolymerization initiator (H), filler (D), coupling agent (E), crosslinking agent (F), and versatile additive (I) in the energy ray-curable resin composition (x2-1), respectively.

[0152]

In the energy ray-curable resin composition (x2-1), one each of the thermosetting components, photopolymerization initiators, fillers, coupling agents, crosslinking agents, and versatile additives may be used alone or two or more of them each in combination. When two or more are used in combination, their combination and ratios can be freely selected.

The contents of the thermosetting component, photopolymerization initiator, filler, coupling agent, crosslinking agent, and versatile additive in the energy ray-curable resin composition (x2-1) are each appropriately adjusted according to the purpose and is not particularly limited.

10 [0153]

The energy ray-curable resin composition (x2-1) improves its handling properties by dilution and thus preferably further contains a solvent.

Examples of the solvent contained in the energy ray-curable resin composition (x2-1) include the same solvent as the solvent in the thermosetting resin composition (x1-1).

15 1).

For the solvent contained in the energy ray-curable resin composition (x2-1), one type may be used alone or two or more types may be used in combination. When two or more solvents are used in combination, their combination and ratios can be freely selected.

20 [0154]

Another component

The energy ray-curable resin composition (x2-1) can contain an appropriate amount of a component other than the curable component, that is, the curing accelerator (C), the filler (D), the coupling agent (E), or the like in addition to the energy ray-curable

component described above as in the case of the thermosetting resin film (x1) described above.

[0155]

Method of manufacturing energy ray-curable resin composition (x2-1)

5           The energy ray-curable resin composition (x2-1) is formed by blending the components for constituting this. The order in which the components are added when blended is not particularly limited, and two or more components may be added simultaneously.

          When a solvent is used, the solvent may be used by mixing with any of the  
10 components to be blended other than the solvent to predilute the component to be blended, or the solvent may be used by mixing with these components to be blended without prediluting any of the components to be blended other than the solvent. The method of mixing the components in blending is not particularly limited and is appropriately selected from known methods, such as a method of mixing by rotating a  
15 stirrer, a stirring blade, or the like; a method of mixing using a mixer; and a method of mixing by applying an ultrasonic wave.

          A temperature and time when the components are added and mixed are not particularly limited as long as each blended component is not degraded, and are appropriately adjusted, but the temperature is preferably from 15 to 30°C.

20 [0156]

Support sheet (Y)

          The support sheet (Y) functions as a support for supporting the curable resin film (x).

          The support sheet (Y) may be composed of only the substrate 11 as illustrated in  
25 Fig. 2 or may be a laminate of the substrate 11 and the PSA layer 21 as illustrated in Fig.

3, or may be a laminate in which the substrate 11, the intermediate layer 31, and the PSA layer 21 are laminated in this order as illustrated in Fig. 4. The laminate in which the substrate 11, the intermediate layer 31, and the PSA layer 21 are laminated in this order is suitable for use as a back grinding tape.

5 [0157]

Hereinafter, the substrate included in the support sheet (Y), the PSA layer and intermediate layer that may be included in the support sheet (Y) will be described.

[0158]

#### Substrate

10 The substrate is in the form of sheet or film, and examples of its constitutional material include various resins below.

Examples of the resin constituting the substrate include polyethylenes, such as low-density polyethylenes (LDPEs), linear low-density polyethylenes (LLDPEs), and high-density polyethylenes (HDPEs); polyolefins other than polyethylenes, such as  
15 polypropylenes, polybutenes, polybutadienes, polymethylpentenes, and norbornene resins; ethylene-based copolymers (copolymers formed using ethylene as a monomer), such as ethylene-vinyl acetate copolymers, ethylene-(meth)acrylic acid copolymers, ethylene-(meth)acrylic ester copolymers, and ethylene-norbornene copolymers; vinyl chloride-based resins (resins formed by using vinyl chloride as a monomer), such as  
20 poly(vinyl chloride) and vinyl chloride copolymers; polystyrenes; polycycloolefins; polyesters, such as poly(ethylene terephthalate), poly(ethylene naphthalate), poly(butylene terephthalate), poly(butylene isophthalate), poly(ethylene-2,6-naphthalene dicarboxylate), and wholly aromatic polyesters in which all the constitutional units have an aromatic cyclic group; copolymers of two or more types of polyesters described  
25 above; poly(meth)acrylic esters; polyurethanes; poly(urethane acrylate); polyimides;

polyamides; polycarbonates; fluororesins; polyacetals; modified poly(phenylene oxide); poly(phenylene sulfide); polysulfones; and poly(ether ketone).

In addition, examples of the resin constituting the substrate also include polymer alloys, such as a mixture of the polyester described above and a resin other than the polyester. The polymer alloy of the polyester and a resin other than the polyester preferably contains a relatively small amount of the resin other than the polyester.

Furthermore, examples of the resin constituting the substrate also include crosslinked resins in which one or two or more of the resins exemplified so far are crosslinked; and modified resins, such as ionomers formed using one or two or more of the resins exemplified so far.

[0159]

One resin constituting the substrate may be used alone or two or more in combination. When two or more resins constitute the substrate, their combination and ratios can be freely selected.

[0160]

The substrate may be composed of only one layer (a single layer) or may be composed of a plurality of two or more layers. When the substrate is composed of a plurality of layers, a plurality of these layers may be identical to or different from each other, and the combination of a plurality of these layers is not particularly limited.

[0161]

A thickness of the substrate is preferably from 5  $\mu\text{m}$  to 1000  $\mu\text{m}$ , more preferably from 10  $\mu\text{m}$  to 500  $\mu\text{m}$ , even more preferably from 15  $\mu\text{m}$  to 300  $\mu\text{m}$ , and still more preferably from 20  $\mu\text{m}$  to 150  $\mu\text{m}$ .

Here, the “thickness of the substrate” means the thickness of the entire substrate; for example, the thickness of a substrate composed of a plurality of layers means the total thickness of all layers composing the substrate.

[0162]

- 5           The substrate is preferably uniformly precise in its thickness, that is, variation in thickness is preferably small in any portion of the substrate. Examples of such a material highly precise in thickness among the constitutional materials described above include polyethylene, polyolefins other than the polyethylene, poly(ethylene terephthalate), and ethylene-vinyl acetate copolymers.

10   [0163]

The substrate may contain a known additive of various types, such as a filler, colorant, antistatic agent, antioxidant, organic lubricant, catalyst, or softener (plasticizer), in addition to the primary constitutional materials, such as the resin.

[0164]

- 15           The substrate may be transparent or opaque or may be colored according to the purpose, or alternatively another layer may be vapor-deposited on the substrate. In addition, when the curable resin film (x) is the energy ray-curable resin film (x2), and when the PSA layer is an energy-curable PSA layer, the substrate preferably transmits an energy ray.

20   [0165]

The substrate can be manufactured by a known method. For example, a substrate containing a resin can be manufactured by molding a resin composition containing the resin.

[0166]

- 25   Pressure sensitive adhesive (PSA) layer

The pressure sensitive adhesive (PSA) layer is in the form of a sheet or film and contains a PSA.

Examples of the PSA include pressure sensitive adhesive resins, such as acrylic resins (PSAs made of a resin having a (meth)acryloyl group), urethane resins (PSAs made of a resin having a urethane bond), rubber-based resins (PSAs made of a resin having a rubber structure), silicone-based resins (PSAs made of a resin having a siloxane bond), epoxy resins (PSAs made of a resin having an epoxy group), poly(vinyl ether)s, and polycarbonates. Among these, an acrylic resin is preferred.

[0167]

In an embodiment of the present invention, the “pressure sensitive adhesive resin” is a concept that includes both a resin having pressure sensitive adhesion and a resin having adhesiveness and includes, for example, not only a resin having pressure sensitive adhesion per se but also a resin that exhibits pressure sensitive adhesion by combined use with another component, such as an additive, and a resin that exhibits adhesiveness by the presence of a trigger, such as heat or water.

[0168]

The PSA layer may be composed of only one layer (a single layer) or may be composed of a plurality of two or more layers. When the PSA layer is composed of a plurality of layers, a plurality of these layers may be identical to or different from each other, and the combination of a plurality of these layers is not particularly limited.

[0169]

A thickness of the PSA layer is preferably from 1  $\mu\text{m}$  to 1000  $\mu\text{m}$ , more preferably from 5  $\mu\text{m}$  to 500  $\mu\text{m}$ , and even more preferably from 10  $\mu\text{m}$  to 100  $\mu\text{m}$ . Here, the “thickness of the PSA layer” means the thickness of the entire PSA layer; for

example, the thickness of a PSA layer composed of a plurality of layers means the total thickness of all layers composing the PSA layer.

[0170]

The PSA layer may be formed using an energy ray-curable PSA or may be  
5 formed using a non-energy ray-curable PSA. The physical properties of the PSA layer formed using an energy ray-curable PSA can be easily adjusted before and after curing.

[0171]

Intermediate layer

The intermediate layer is in the form of a sheet or film, and the constitutional  
10 material is appropriately selected according to the purpose and is not particularly limited. For example, a shape of each of the bumps present on the semiconductor surface may be reflected on the protective film covering the semiconductor surface, and this may deform the protective film (X). When the purpose is to prevent such deformation of the protective film (X), examples of a preferred constitutional material of the intermediate  
15 layer include urethane (meth)acrylates from the viewpoints of increasing conformability to unevenness, achieving good bump penetration, and further improving the bondability of the intermediate layer.

[0172]

The intermediate layer may be composed of only one layer (a single layer) or  
20 may be composed of a plurality of two or more layers. When the intermediate layer is composed of a plurality of layers, a plurality of these layers may be identical to or different from each other, and the combination of a plurality of these layers is not particularly limited.

[0173]

A thickness of the intermediate layer can be appropriately adjusted according to the height of the bump of the semiconductor surface to be protected but is preferably from 50  $\mu\text{m}$  to 600  $\mu\text{m}$ , more preferably from 70  $\mu\text{m}$  to 500  $\mu\text{m}$ , and even more preferably from 80  $\mu\text{m}$  to 400  $\mu\text{m}$  from the viewpoint that the effect of bumps with  
5 relatively high height can also be easily absorbed. Here, the “thickness of the intermediate layer” means the thickness of the entire intermediate layer; for example, the thickness of a PSA layer composed of a plurality of layers means the total thickness of all layers composing the intermediate layer.

[0174]

10           Next, a method of manufacturing a sheet for forming a protective film will be described.

[0175]

Method of manufacturing sheet for forming protective film

          The sheet for forming a protective film can be manufactured by sequentially  
15 laminating the layers described above to form the corresponding arrangement.

          For example, in a case where the PSA layer or intermediate layer is laminated on the substrate in manufacturing the support sheet, the PSA layer or intermediate layer can be laminated by applying a PSA composition or a composition for forming an intermediate layer onto the substrate, and drying as necessary or irradiating with an  
20 energy ray.

          Examples of the application method include a spin coating method, spray coating method, bar coating method, knife coating method, roll coating method, roll knife coating method, blade coating method, die coating method, and gravure coating method.

25   [0176]

On the other hand, for example, in a case where the curable resin film (x) is further laminated on the PSA layer already laminated on the substrate, the thermosetting resin composition (x1-1) or the energy ray-curable resin composition (x2-1) is applied onto the PSA layer, and the curable resin film (x) can be directly formed.

- 5 Likewise, in a case where the PSA layer is further laminated on the intermediate layer already laminated on the substrate, a PSA composition is applied onto the intermediate layer, and the PSA layer can be directly formed.

[0177]

- In a case where a continuous two-layer laminated structure is thus formed using  
10 any of the compositions, a composition is further applied onto the layer formed from the composition, and a layer can be newly formed. However, the continuous two-layered laminated structure is formed preferably by the following procedure: of the two layers in the laminated structure, the layer to be laminated later is formed in advance on another release film using the composition; and an exposed surface of this formed layer, the  
15 exposed surface opposite from the side in contact with the release film, is bonded to an exposed surface of another layer already formed. In this case, the composition is preferably applied to a release-treated surface of the release film. The release film is removed as necessary after formation of the laminated structure.

[0178]

- 20 Method of manufacturing semiconductor wafer with protective film using sheet for forming protective film

A method of manufacturing a semiconductor wafer with a protective film according to an embodiment of the present invention is performed using the sheet for forming a protective film according to an embodiment of the present invention described  
25 above.

Specifically, the method includes:

(S1) preparing a semiconductor wafer having a bump-formed surface including a plurality of bumps;

(S2) bonding the sheet for forming a protective film according to an embodiment of the present invention described above to the bump-formed surface of the semiconductor wafer with pressing the sheet to the bump-formed surface of the semiconductor wafer using the curable resin film (x) as a bonding surface; and

(S3) curing the curable resin film (x) to form the protective film (X).

Hereinafter, the method of manufacturing a semiconductor wafer with a protective film according to an embodiment of the present invention will be described with detailed descriptions of a semiconductor wafer to which an embodiment of the present invention is applicable.

[0179]

Step (S1)

In step (S1), a semiconductor wafer having a bump-formed surface including a plurality of bumps is prepared.

An example of a semiconductor wafer having a bump-formed surface provided with a plurality of bumps, the semiconductor wafer to be used in the method of manufacturing a semiconductor wafer with a protective film according to an embodiment of the present invention, is illustrated in Fig. 5. A semiconductor wafer 40 provided with bumps includes a plurality of bumps BM on a bump-formed surface (circuit surface) 41a of a semiconductor wafer 41.

In the following descriptions, the “semiconductor wafer provided with bumps” is also referred to as a “wafer with bumps”. The “semiconductor wafer” is also referred to simply as a “wafer”.

[0180]

The wafer 41 has, for example, a circuit, such as wiring, a capacitor, a diode, and a transistor, formed on the surface. A material of the wafer is not particularly limited, and examples include silicon wafers, silicon carbide wafers, compound semiconductor  
5 wafers, sapphire wafers, and glass wafers.

[0181]

A size of the wafer 41 is not particularly limited but is usually 8 inches (200 mm in diameter) or greater and preferably 12 inches (300 mm in diameter) or greater from the viewpoint of increasing batch processing efficiency. A shape of the wafer is not limited  
10 to a circle and may be, for example, a quadrangle shape, such as a square or a rectangle. In the case of a quadrangle shape wafer, for the size of the wafer 41, the length of the longest side is not shorter than the size (diameter) described above from the viewpoint of increasing batch processing efficiency.

[0182]

15 A thickness of the wafer 41 is not particularly limited but is preferably from 100  $\mu\text{m}$  to 1000  $\mu\text{m}$ , more preferably from 200  $\mu\text{m}$  to 900  $\mu\text{m}$ , and even more preferably from 300  $\mu\text{m}$  to 800  $\mu\text{m}$  from the viewpoint of suppression of warpage of the wafer 41 associated with curing the curable resin film (x).

[0183]

20 A shape of the bump BM is not particularly limited and may be any shape as long as the bump can be brought into contact with an electrode or the like on the substrate for mounting a chip and be fixed. For example, in Fig. 5, the bump BM has a ball-shape, but the bump BM may be a spheroid. The spheroid may be, for example, a spheroid extended in the direction perpendicular to the bump-formed surface 41a of the

wafer 41 or may be a spheroid extended in the direction horizontal to the bump-formed surface 41a of the wafer 41.

In addition, as illustrated in Fig. 6, the bump BM may have a pillar (column)-shape.

5           Examples of the bump BM material include solder.

[0184]

Here, an embodiment of the present invention is applicable to semiconductor wafers having fine-pitched bumps specified by the requirements described below.

That is, in an embodiment of the present invention, the protective film (X) is  
10   formed on a bump-formed surface of a semiconductor wafer having a fine-pitched bumps using the sheet for forming a protective film to prevent crushing or deformation of the fine-pitched bumps and avoid a short circuit between bumps is prevented. In other words, the semiconductor wafer to which an embodiment of the present invention is applicable is a semiconductor wafer having fine-pitched bumps that may short-circuit due to  
15   crushing or deformation of the bumps in a case where the protective film (X) is not formed.

In other words, the semiconductor wafer described below is a semiconductor wafer having fine-pitched bumps that may short-circuit due to crushing or deformation of the bumps in a case where the protective film (X) is not formed.

20   [0185]

Semiconductor wafer

The sheet for forming a protective film according to an embodiment of the present invention is to be used to form a protective film (X) on a bump-formed surface of a semiconductor wafer satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) below.

In addition, the method of manufacturing a semiconductor wafer with a protective film according to an embodiment of the present invention is performed using a semiconductor wafer satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) below:

• Requirement ( $\alpha 1$ ): The width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to 5 350  $\mu m$ ; and

• Requirement ( $\alpha 2$ ): The pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I) below:

$$[(BM_p)/(BM_w)] \leq 1.0 \quad (I).$$

[0186]

10 Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) above are indices indicating that the wafer is a semiconductor wafer having fine-pitched bumps. That is, they indicate that a short circuit due to crushing or deformation of bumps is likely to occur.

To illustrate the definitions of the pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump, an enlarged top view of three bumps  $BM_a$ ,  $BM_b$ , 15 and  $BM_c$  formed on the bump-formed surface of the wafer 41 is illustrated in Fig. 7.

The pitch ( $BM_p$ ) of the bumps is the shortest distance between two bumps. In Fig. 7, the shortest distance between the bump  $BM_a$  and the bump  $BM_b$  is  $P_1$ . In addition, the shortest distance between the bump  $BM_b$  and the bump  $BM_c$  is  $P_2$ .

The width ( $BM_w$ ) of the bump is the length of a straight line  $b_1$ - $b_2$  connecting a 20 point  $b_1$  and a point  $b_2$ ,  $b_1$  being an intersection point of a straight line  $P_1$  with the bump  $BM_b$ ,  $b_2$  being an intersection point of a straight line  $P_2$  with the bump  $BM_b$ , and the straight line  $P_1$  being a line connecting the bump  $BM_a$  with the bump  $BM_b$ , and the straight line  $P_2$  being a line connecting the bump  $BM_b$  with the bump  $BM_c$ .

The pitch ( $BM_P$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump can be measured based on the above definitions, for example, by optical microscope observation.

[0187]

- 5            If Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) above are satisfied between at least any one pair of bumps among the plurality of bumps present on the wafer, a short circuit may occur between the bumps due to the fine pitch between the bumps.

Thus, the wafer to which an embodiment of the present invention is applicable is a wafer satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ) above between at least any one pair of

- 10       bumps among the plurality of bumps present on the wafer.

[0188]

Here, the width ( $BM_w$ ) (unit:  $\mu m$ ) specified by Requirement ( $\alpha 1$ ) is from 20  $\mu m$  to 350  $\mu m$ . That is, according to an embodiment of the present invention, the method is also applicable to wafers including a plurality of bumps with a small bump width ( $BM_w$ )

- 15       20  $\mu m$  or greater and less than 150  $\mu m$  (particularly from 20  $\mu m$  to 100  $\mu m$ ). In other words, an embodiment of the present invention is also applicable to wafers with fine pitch and a plurality of microbumps. In addition, an embodiment of the present invention is also applicable to wafers including a plurality of bumps with a large bump width ( $BM_w$ ) of 150  $\mu m$  to 350  $\mu m$ . In other words, an embodiment of the present invention is
- 20       also applicable to wafers including a plurality of bumps with fine pitch and large width.

In wafers including a plurality of bumps with fine pitch and large width, a short circuit between bumps is likely to occur, but according to an embodiment of the present invention, the method can prevent a short circuit between bumps in such wafers.

[0189]

Here, the value of  $[(BM_p)/(BM_w)]$  specified by Requirement ( $\alpha 2$ ) is one of indices indicating the likelihood of a short circuit between bumps, and this value may be 0.9 or lower or 0.8 or lower.

[0190]

5 Here, the wafer may further satisfy Requirement ( $\alpha 3a$ ) below or Requirement ( $\alpha 3b$ ) below.

- Requirement ( $\alpha 3a$ ): The height ( $BM_h$ ) of the bump and the width ( $BM_w$ ) of the bump satisfy Relationship (IIIa) below:

$$0.2 \leq [(BM_h)/(BM_w)] \leq 1.0 \quad (IIIa).$$

10 • Requirement ( $\alpha 3b$ ): The height ( $BM_h$ ) of the bump and the width ( $BM_w$ ) of the bump satisfy Relationship (IIIb) below:

$$0.5 \leq [(BM_h)/(BM_w)] \leq 5.0 \quad (IIIb).$$

[0191]

Requirement ( $\alpha 3a$ ) above is an index indicating that the bump is a ball bump; 15 the value of  $[(BM_h)/(BM_w)]$  closer to 1.0 indicates that the bump is closer to a true sphere, and the value closer to 0.2 indicates that the bump is a spheroid extended in the direction horizontal to the bump-formed surface 41a of the wafer 41.

In dividing the semiconductor wafer having such ball bumps into individual semiconductor chips and electrically connecting the semiconductor chip and a wiring 20 board via ball bumps, the ball bumps may be crushed and spread in the lateral direction, and the ball bumps may come into contact with each other and may cause a short circuit problem. In addition, to meet the demand for even higher density mounting, three-dimensional high-density mounting is also under study, in which semiconductor packages are stacked in the height direction; in this case, ball bumps are gradually 25 crushed by the self-weight of the semiconductor packages, and this may lead to a short

circuit. According to an embodiment of the present invention, the method can prevent a short circuit due to contact between the ball bumps.

[0192]

Requirement ( $\alpha 3b$ ) above is an index indicating that the bump is a pillar bump;  
5 the value of  $[(BM_h)/(BM_w)]$  closer to 5.0 indicates that the bump is a pillar bump with high aspect ratio, and the value closer to 0.5 indicates that the pillar is a pillar bump with low aspect ratio.

In dividing the semiconductor wafer having such pillar bumps into individual semiconductor chips and electrically connecting the semiconductor chip and a wiring  
10 board via pillar bumps, the pillar bumps may be deformed and bent, and the pillar bumps may come into contact with each other and may cause a short circuit problem. In addition, the pillar bumps may be deformed and bent, and this also may cause a connection failure problem. Furthermore, to meet the demand for even higher density mounting, three-dimensional high-density mounting is also under study, in which  
15 semiconductor packages are stacked in the height direction; in this case, pillar bumps are gradually deformed by the self-weight of the semiconductor packages, and this may lead to a short circuit. According to an embodiment of the present invention, the method can prevent a short circuit due to contact between the pillar bumps. Moreover, an embodiment of the present invention can also prevent the connection failure that may be  
20 caused by deformation of the pillar bumps.

[0193]

The height ( $BM_h$ ) of the bump means, when attention is focused on one bump, a distance of a straight line connecting an intersection point of the bump on the bump-formed surface and a site of the bump at the farthest position from the bump-formed  
25 surface.

The height ( $BM_h$ ) of the bump may be specifically a value specified by Requirement ( $\alpha 4$ ) below.

- Requirement ( $\alpha 4$ ): The height ( $BM_h$ ) of the bump is from 15  $\mu m$  to 300  $\mu m$ .

That is, an aspect of the present invention is also applicable to wafers including  
5 a plurality of bumps with a low bump height ( $BM_h$ ) of 20  $\mu m$  or higher and lower than 150  $\mu m$  (particularly from 20  $\mu m$  to 100  $\mu m$ ). In addition, an aspect of the present invention is also applicable to wafers including a plurality of bumps with a high bump height ( $BM_h$ ) of 150  $\mu m$  to 350  $\mu m$ .

The height ( $BM_h$ ) of the bump can be measured, for example, by cutting the  
10 semiconductor wafer with a protective film in the direction perpendicular to the bump-formed surface and passing through the center of the bump, and observing the cut cross-section with an optical microscope.

[0194]

Step (S2)

15 Step (S2) is schematically illustrated in Fig. 8.

In step (S2), the sheet 1 for forming a protective film according to an embodiment of the present invention described above is bonded to the bump-formed surface 41a of the semiconductor wafer 41 with pressing the sheet 1 to the bump-formed surface 41a of the semiconductor using the curable resin film (x) as a bonding surface.

20 This allows the bump-formed surface 41a of the semiconductor wafer 41 to be covered with the curable resin film (x) as well as the curable resin film (x) to fill the space between the plurality of bumps BM.

[0195]

The pressing force when the sheet 1 for forming a protective film is bonded to  
25 the bump-formed surface 41a of the semiconductor wafer 41 is preferably from 1 kPa to

200 kPa, more preferably from 5 kPa to 150 kPa, and even more preferably from 10 kPa to 100 kPa from the viewpoint of achieving good filling of the curable resin film (x) between the plurality of bumps BM.

The pressing force when the sheet 1 for forming a protective film is bonded to the bump-formed surface 41a of the semiconductor wafer 41 may be appropriately changed in a period from the initial stage to the final stage of the bonding. For example, from the viewpoint of achieving better filling of the curable resin film (x) between the plurality of bumps BM, the pressing force is preferably low at the initial stage of the bonding and gradually increased.

10 [0196]

In addition, when the sheet 1 for forming a protective film is bonded to the bump-formed surface 41a of the semiconductor wafer 41, in the case where the curable resin film (x) is the thermosetting resin film (x1), heating is preferably performed from the viewpoint of achieving even better filling of the curable resin film (x) between the plurality of bumps BM. When the curable resin film (x) is the thermosetting resin film (x1), the fluidity of the thermosetting resin film (x1) is temporarily increased by heating, and the thermosetting resin film (x1) is cured by continued heating. Thus, heating is performed within a range in which the fluidity of the thermosetting resin film (x1) is improved, and this allows the thermosetting resin film (x1) to be easily distributed between the plurality of bumps BM, and this further improves the filling properties of the thermosetting resin film (x1) between the plurality of bumps BM.

Specific heating temperature (bonding temperature) is preferably from 50°C to 150°C, more preferably from 60°C to 130°C, and even more preferably from 70°C to 110°C.

The heating treatment performed on the thermosetting resin film (x1) is not included in the curing treatment of the thermosetting resin film (x1).

[0197]

Furthermore, when the sheet 1 for forming a protective film is bonded to the bump-formed surface 41a of the semiconductor wafer 41, the bonding may be performed in a reduced pressure environment. This creates a negative pressure between the plurality of bumps BM and allows the curable resin film (x) to be easily distributed between the plurality of bumps BM. As a result, this is more likely to improve the filling properties of the curable resin film (x) between the plurality of bumps BM. The specific pressure of the reduced pressure environment is preferably from 0.001 kPa to 50 kPa, more preferably from 0.01 kPa to 5 kPa, and even more preferably from 0.05 kPa to 1 kPa.

[0198]

Step (S3)

After performing step (S2), step (S3) is performed. Specifically, as illustrated in Fig. 9, the curable resin film (x) is cured to form a semiconductor wafer with a protective film.

The protective film (X) formed by curing the curable resin film (x) is stronger than the curable resin film (x) at ordinary temperature (23°C). Thus, the bump neck is well protected by forming the protective film (X).

In addition, in an embodiment of the present invention, the method uses the sheet for forming a protective film, the sheet satisfying Requirements (β1) to (β3) above, thus crushing or deformation of the bumps can be prevented for the semiconductor wafers having fine-pitched bumps that are prone to short-circuit due to crushing or deformation as described above, and a short circuit due to contact between the bumps can be avoided.

[0199]

Curing of the curable resin film (x) can be performed by any of the curing of thermal curing and energy ray irradiation according to the type of the curable component contained in the curable resin film (x).

5 For the conditions in case of the thermal curing, the curing temperature is preferably from 90°C to 200°C, and the curing time is preferably from 1 hour to 3 hours.

The conditions in case of energy ray irradiation are appropriately set according to the type of energy ray to be used; for example, when ultraviolet light is used, the illuminance is preferably from 170 mW/cm<sup>2</sup> to 250 mw/cm<sup>2</sup>, and the amount of light is  
10 preferably from 300 mJ/cm<sup>2</sup> to 3000 mJ/cm<sup>2</sup>.

[0200]

Here, in the process of curing the curable resin film (x) to form the protective film (X), the curable resin film (x) is preferably the thermosetting resin film (x1) from the viewpoint of removal of an air bubble or the like that may enter during filling  
15 between the plurality of bumps BM with the curable resin film (x) in step (S2). That is, when the curable resin film (x) is the thermosetting resin film (x1), heating increases the fluidity of the thermosetting resin film (x1) temporarily, and with continuous heating, the thermosetting resin film (x1) is cured. Utilizing this phenomenon, the method facilitates removal of an air bubble or the like that may enter during filling between the plurality of  
20 bumps BM with the thermosetting resin film (x1) when the fluidity of the thermosetting resin film (x1) is increased. This can provide curing of the thermosetting resin film (x1) when the thermosetting resin film (x1) has the better filling properties between the plurality of bumps BM.

In addition, from the viewpoint of shortening the curing time, the curable resin  
25 film (x) is preferably the energy ray-curable resin film (x1).

[0201]

The support sheet (Y) is peeled off before curing the curable resin film (x), then the curable resin film (x) is cured to form the protective film (X), and this provides the semiconductor wafer with a protective film. However, the method is not limited to such an aspect; the semiconductor wafer with a protective film may also be produced by curing the curable resin film (x) to form the protective film (X) and then peeling off the support sheet (Y).

In addition, the surface opposite from the bump-formed surface 41a of the semiconductor wafer 41 (i.e., the back surface of the semiconductor wafer 41) may be ground to reduce the thickness of the semiconductor wafer 41 (back grinding processing) without peeling off the support sheet (Y). The back grinding processing may be performed before curing the curable resin film (x) or may be performed after curing the curable resin film (x).

Furthermore, when the back grinding processing is performed, the support sheet (Y) is preferably a back grinding tape from the viewpoint of achieving good performance of the back grinding processing.

[0202]

In addition, after curing the curable resin film (x), the protective film (X) covering the top of the bump or the protective film (X) deposited on a portion of the top of the bump may be removed to perform a treatment to expose the bump top.

Examples of the exposure treatment to expose the top of the bump include etching treatment, such as wet etching treatment and dry etching treatment.

Here, examples of the dry etching treatment include plasma etching treatment.

In a case where the top of the bump is not exposed on the surface of the protective film, the exposure treatment may be performed for the purpose of causing retraction of the protective film until the top of the bump is exposed.

[0203]

#### 5 Method of manufacturing semiconductor chip with protective film

A method of manufacturing a semiconductor chip with a protective film according to an embodiment of the present invention includes:

(T1) performing the method of manufacturing a semiconductor wafer with a protective film according to an embodiment of the present invention to produce a

10 semiconductor wafer with a protective film; and

(T2) dividing the semiconductor wafer with a protective film into individual pieces.

[0204]

#### Step (T1)

15 In step (T1), the method of manufacturing a semiconductor wafer with a protective film according to an embodiment of the present invention described above is performed to produce a semiconductor wafer with a protective film.

[0205]

#### Step (T2)

20 In step (T2), the semiconductor wafer with a protective film produced in step (T1) is divided into individual pieces.

The method of dividing the wafer into pieces is not particularly limited, and a known method of dividing can be appropriately adopted. Specifically, examples include laser dicing, blade dicing, and Stealth Dicing (trade name).

25 [0206]

The method may include forming a back surface protective film on a back surface of the semiconductor wafer (surface opposite from the bump-formed surface) with a protective film before performing step (T1).

[0207]

## 5 Method of manufacturing semiconductor package

A method of manufacturing a semiconductor package according to an embodiment of the present invention includes:

(U1) performing the method of manufacturing a semiconductor chip with a protective film according to an embodiment of the present invention to produce a

10 semiconductor chip with a protective film; and

(U2) electrically connecting a wiring board and the semiconductor chip with a protective film via the bumps.

[0208]

Step (U1)

15 In step (U1), the method of manufacturing a semiconductor chip with a protective film according to an embodiment of the present invention described above is performed to produce a semiconductor chip with a protective film.

[0209]

Step (U2)

20 In step (U2), as illustrated in Fig. 10, a wiring board (Z) having wirings Z1 and a semiconductor chip (CP) with a protective film are electrically connected via the bumps BM.

In more detail, the bump-formed surface of the semiconductor chip CP with a protective film and the surface of the wiring board (Z) on which the wirings Z1 are

25 formed are faced with each other via the bumps BM and heated in that state (hereinafter

also referred to as “heating connection”). This can provide good electrical connection between the tops of the bumps BM and the wirings Z1.

In addition, in an embodiment of the present invention, the method uses the semiconductor chip produced from the semiconductor wafer having fine-pitched bumps  
5 that may short-circuit due to crushing or deformation of the bumps. Nevertheless, the sheet for forming a protective film according to an embodiment of the present invention satisfies Requirements ( $\beta 1$ ) to ( $\beta 3$ ) above, especially Requirement ( $\beta 2$ ) above among them, and thus the method can prevent contact between the bumps due to crushing or deformation of the bumps in the heating connection and can avoid a short circuit due to  
10 contact between the bumps.

For the conditions for the heating connection, for example, the temperature is from 250°C to 270°C, and the time is from 30 seconds to 5 minutes.

[0210]

Step (U3)

15 The method of manufacturing a semiconductor package according to an aspect of the present invention further includes:

(U3) filling an underfill material between the wiring board and the semiconductor chip with a protective film.

In an embodiment of the present invention, the method can prevent contact  
20 between the bumps due to crushing or deformation of the bumps as described above. In other words, the method can prevent the bumps from coming into close proximity with each other due to crushing or deformation of the bumps. When the bumps come into close proximity, the gaps between the bumps are narrow, and thus this has made it difficult to fill the gaps with an underfill material in the related art. However, in an  
25 embodiment of the present invention, the method also prevents the close proximity of the

bumps and thus can achieve good filling of an underfill material between the protective film (X) and the wiring board (Z) including the gaps between the bumps.

Examples

[0211]

5           The present invention will be specifically described with reference to examples below, but the present invention is not limited to the following examples.

[0212]

Method of measuring various physical properties

Physical property values in the examples and comparative examples below are  
10 values measured by the following methods.

[0213]

Weight average molecular weight

Weight average molecular weight (Mw) was measured using a gel permeation chromatograph (product name “HLC-8020”, available from Tosoh Corporation) under  
15 the following conditions, and values measured in terms of standard polystyrene were used.

Measurement conditions

- Column: “TSK guard column HXL-L”, “TSK gel G2500HXL”, “TSK gel G2000HXL”, and “TSK gel G1000HXL” (all available from Tosoh Corporation)  
20 connected in sequence
- Column temperature: 40°C
- Developing solvent: tetrahydrofuran
- Flow rate: 1.0 mL/min

[0214]

25 Measurement of thickness of each layer

Thicknesses other than the thickness ( $X_T$ ) of the protective film (after curing) were measured using a constant pressure thickness meter (Model number “PG-02J”, in accordance with standard specifications JIS K6783, Z1702, and Z1709).

[0215]

## 5 Glass transition temperature

The glass transition temperature ( $T_g$ ) of a polymer component (A) described later was determined by measuring using a differential scanning calorimeter (PYRIS Diamond DSC) available from PerkinElmer Co., Ltd. with a temperature profile from -70°C to 150°C at a temperature increase or decrease rate of 10°C/min to determine the

10 inflection point.

[0216]

Epoxy equivalent weight

The epoxy equivalent weight was measured in accordance with JIS K 7236: 2009.

15 [0217]

Average particle size

A particle to be measured was dispersed ultrasonically in water, the particle size distribution of the particles was measured on a volume basis with a dynamic light scattering particle size distribution meter (LB-550, available from Horiba Ltd.), and the median diameter ( $D_{50}$ ) was determined as the average particle size.

20

[0218]

Examples 1 to 4 and Comparative Examples 1 to 2

The thermosetting resin composition (x1-1) used in manufacturing the thermosetting resin film (x1) used in the examples was prepared by the following

25 method.

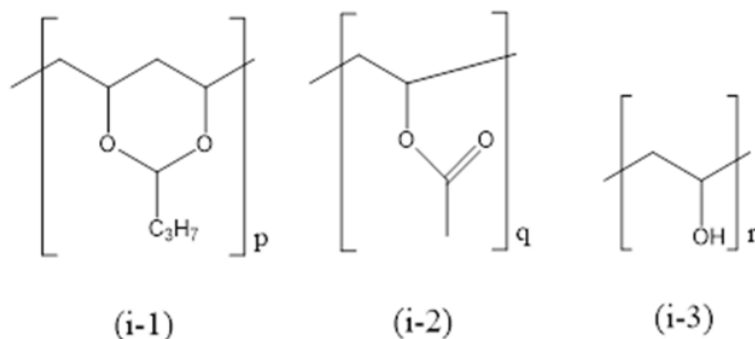
[0219]

Raw materials for thermosetting resin composition (x1-1)

Polymer component (A)

A poly(vinyl butyral) having constitutional units represented by Formulas (i-1),  
5 (i-2), and (i-3) below (S-LEC (trade name) B BL-10, available from Sekisui Chemical  
Co., Ltd., weight average molecular weight 25000, glass transition temperature 59°C,  
and in the formula below, p is from 68 to 74 mol%, q is from 1 to 3 mol%, and r is about  
28 mol%) was used.

[Chem. 2]



10

[0220]

Epoxy resin (B1)

The following two epoxy resins were used:

• Epoxy resin (B1-1): Liquid bisphenol A-type epoxy resin (EPICLON (trade  
15 name) EXA-4850-1000, available from DIC Corporation, epoxy equivalent weight from  
404 to 412 g/eq)

• Epoxy resin (B1-2): Dicyclopentadiene-type epoxy resin (EPICLON (trade  
name) HP-7200, available from DIC Corporation, equivalent weight from 254 to 264  
g/eq)

20 [0221]

Thermal curing agent (C)

A novolac-type phenolic resin (Shonol (trade name) BRG-556, available from Showa Denko K.K.) was used.

[0222]

5 Curing accelerator (C)

2-Phenyl-4,5-dihydroxymethylimidazole (Curezol (trade name) 2PHZ, available from Shikoku Chemicals Corporation) was used.

[0223]

Filler (E)

10 A spherical silica modified with an epoxy group (Admanano (trade name) YA050C-MKK, available from Admatechs Company Limited, average particle size 0.05  $\mu\text{m}$ ) was used.

[0224]

Preparation of thermosetting resin composition (x1-1)

15 Thermosetting resin compositions (x1-1) with a concentration of 55 mass% of active components (solid contents) were prepared by dissolving or dispersing the polymer component (A), the epoxy resin (B1-1), the epoxy resin (B1-2), the thermal curing agent (B2), the curing accelerator (C), and the filler (D) in methyl ethyl ketone and stirring at 23°C to give contents shown below based on the total amount (100  
20 mass%) of the thermosetting resin composition (x1-1).

In Examples 1 and 2, the protective film (X) was formed using the thermosetting resin composition (x1-1) prepared with Formulation 1 shown below. In addition, in Examples 3 and 4, the protective film (X) was formed using the thermosetting resin composition (x1-1) prepared with Formulation 2 shown below.

25 Formulation 1

- Polymer component (A): 41.4 mass%
- Epoxy resin (B1-1): 23.2 mass%
- Epoxy resin (B1-2): 15.2 mass%
- Thermal curing agent (B2): 11.2 mass%
- 5      • Curing accelerator (C): 0.2 mass%
- Filler (D): 8.8 mass%

#### Formulation 2

- Polymer component (A): 19.9 mass%
- Epoxy resin (B1-1): 33.1 mass%
- 10      • Epoxy resin (B1-2): 21.7 mass%
- Thermal curing agent (B2): 16.1 mass%
- Curing accelerator (C): 0.2 mass%
- Filler (D): 9.0 mass%

[0225]

#### 15      Manufacture of thermosetting resin film (x1)

The thermosetting resin composition (x1-1) prepared with Formulation 1 was applied to a release-treated surface of a release material (SP-PET 381031, available from Lintec Corporation, thickness 38  $\mu\text{m}$ ) made of a poly(ethylene terephthalate) and having the release-treated surface release-treated with silicone and dried by heating at 120°C for 20      2 minutes, and a thermosetting resin film (x1: Formulation 1) with a thickness of 30  $\mu\text{m}$  was obtained. In addition, a thermosetting resin film (x1: Formulation 2) with a thickness of 50  $\mu\text{m}$  was produced by the same method except that the thermosetting resin composition (x1-1) was changed to the thermosetting resin composition (x1-1) prepared in Formulation 2.

25      [0226]

## Manufacture of protective film

A bonding tape (E-8510HR, available from Lintec Corporation) in which a substrate (thickness: 100  $\mu\text{m}$ ), an intermediate layer (thickness: 400  $\mu\text{m}$ ), and a PSA layer (thickness: 10  $\mu\text{m}$ ) were laminated in this order was used as a support sheet (Y), the  
5 PSA layer of this bonding tape and the thermosetting resin film (x1: Formulation 1) with a thickness of 30  $\mu\text{m}$  formed on the release material were bonded together, and a sheet 1 for forming a protective film, the sheet 1 including the support sheet (Y), the thermosetting resin film (x1), and the release material laminated in this order, was manufactured.

10 Also from the thermosetting resin film (x1: Formulation 2) with a thickness of 50  $\mu\text{m}$ , a sheet 2 for forming a protective film was manufactured by a similar procedure.  
[0227]

## Measurement of modulus of elasticity in tension $E'$ of protective film (X)

After curing the thermosetting resin film (x1), the modulus of elasticity in  
15 tension,  $E'$ , of the protective film (X) was measured by the following method.

First, a sample with a thickness of 0.18 mm, a width of 4.5 mm, and a length of 20.0 mm was produced by stacking six thermosetting resin films (x1: Formulation 1) with a thickness of 30  $\mu\text{m}$ . The sample was heat-treated in a pressure oven (RAD-9100 available from Lintec Corporation) under heating conditions of a temperature of 130°C, a  
20 time of 2 h, and an internal pressure in the oven of 0.5 MPa, and a protective film (X) was obtained.

The protective film (X) was then measured for the modulus of elasticity in tension,  $E'$  (23°C), of the protective film (X) using a dynamic viscoelasticity measuring device (trade name “DMA Q800”, available from TA instruments) in the tension mode,  
25 at a frequency of 11 Hz, and 23°C under atmospheric atmosphere. In addition, the

modulus of elasticity in tension,  $E'$  (260°C), of the protective film (X) was measured under the same conditions except that the temperature was set at 260°C.

For the thermosetting resin film (x1: Formulation 2), a protective film (X) was produced by the same procedure except that four thermosetting resin films (x1:

- 5 Formulation 2) with a thickness of 50  $\mu\text{m}$  were stacked to a thickness of 0.20 mm, and the modulus of elasticity in tension,  $E'$  (23°C), of the protective film (X) and the modulus of elasticity in tension,  $E'$  (260°C), of the film (X) were measured.

[0228]

#### Short circuit evaluation

- 10 The release material was removed from the sheet for forming a protective film produced above, and the surface (exposed surface) of the thermosetting resin layer, the surface exposed by this procedure, was press-bonded to a bump-formed surface of a wafer with ball bumps, and thereby the sheet for forming a protective film was bonded to the bump-formed surface of the semiconductor wafer. At this time, the sheet for forming
- 15 a protective film was bonded using a bonding device (roller laminator, “RAD-3510 F/12” available from Lintec Corporation) with heating thermosetting resin film (x1) under conditions of a table temperature of 90°C, a bonding rate of 2 mm/sec, and a bonding pressure of 0.5 MPa. The details (Requirements ( $\alpha 1$ ), ( $\alpha 2$ ), ( $\alpha 3a$ ), and ( $\alpha 4$ )) of the wafers with ball bumps, the wafers including the bonded sheets 1 or 2 for forming a protective
- 20 film, are shown in Table 1.

The support sheet (Y) of the sheet for forming a protective film was then peeled off by ultraviolet light irradiation using an RAD-2700 available from Lintec Corporation.

The wafers with bumps to which the thermosetting resin film (x1) was bonded were heat-treated in a pressure oven (RAD-9100 available from Lintec Corporation)

- 25 under heating conditions of a temperature of 130°C, a time duration of 2 h, and an

internal pressure in the oven of 0.5 MPa to thermally cure the thermosetting resin film (x1), and semiconductor wafers with the protective film (X) (Examples 1 to 4) were produced.

The thickness ( $X_T$ ) of the protective film (X) was measured by cutting the semiconductor wafer with the protective film (X) in the direction perpendicular to the bump-formed surface and passing through the center of the bump, and observing the cross-section with an optical microscope after cutting.

The bump-formed surface of the semiconductor wafer with the protective film (X) and the wiring-formed surface of the wiring board were then faced with each other via the bumps and subjected in that state to heat treatment (heating connection) at 260°C for 1 minute, and the presence or absence of contact between the bumps (presence or absence of short circuit) was evaluated.

As a comparison test, wafers with bumps similar to those in Examples 1 and 3 as well as Examples 2 and 4 but in which no protective film (X) was formed were subjected to the heating connection and the presence or absence of a short circuit was evaluated (Comparative Examples 1 and 2).

The results are shown in Table 1.

[0229]

Table 1

Table 1

|                                        | Requirement | Example 1     | Example 2     | Example 3     | Example 4     | Comparative Example 1 | Comparative Example 2 |
|----------------------------------------|-------------|---------------|---------------|---------------|---------------|-----------------------|-----------------------|
| Sheet for forming protective film used | -           | Formulation 1 | Formulation 1 | Formulation 2 | Formulation 2 | -                     | -                     |

|                             |                                                                                                              |       |                     |                     |                     |                     |      |      |
|-----------------------------|--------------------------------------------------------------------------------------------------------------|-------|---------------------|---------------------|---------------------|---------------------|------|------|
| Wafer<br>with ball<br>bumps | Bump width<br>(BM <sub>w</sub> ) (unit:<br>μm)                                                               | (α1)  | 320                 | 320                 | 320                 | 320                 | 320  | 320  |
|                             | Bump pitch<br>(BM <sub>p</sub> ) (unit:<br>μm)                                                               | -     | 130                 | 220                 | 130                 | 220                 | 130  | 220  |
|                             | [(BM <sub>p</sub> )/(BM <sub>w</sub> )]                                                                      | (α2)  | 0.41                | 0.70                | 0.41                | 0.70                | 0.41 | 0.70 |
|                             | Height (BM <sub>h</sub> )<br>(unit: μm) of<br>bump                                                           | (α4)  | 250                 | 250                 | 250                 | 250                 | 250  | 250  |
|                             | [(BM <sub>h</sub> )/(BM <sub>w</sub> )]                                                                      | (α3a) | 0.78                | 0.78                | 0.78                | 0.78                | 0.78 | 0.78 |
| Protective<br>film (X)      | Modulus of<br>elasticity in<br>tension, E'<br>(23°C), of<br>protective film<br>(after curing)<br>(unit: Pa)  | (β1)  | 2 x 10 <sup>8</sup> | 2 x 10 <sup>8</sup> | 3 x 10 <sup>9</sup> | 3 x 10 <sup>9</sup> | -    | -    |
|                             | Modulus of<br>elasticity in<br>tension, E'<br>(260°C), of<br>protective film<br>(after curing)<br>(unit: Pa) | (β2)  | 5 x 10 <sup>6</sup> | 5 x 10 <sup>6</sup> | 1 x 10 <sup>7</sup> | 1 x 10 <sup>7</sup> | -    | -    |
|                             | Thickness of<br>thermosetting<br>resin film (x1)                                                             | -     | 30                  | 30                  | 50                  | 50                  | -    | -    |
|                             | Thickness (X <sub>T</sub> )<br>(unit: μm) of<br>protective film<br>(after curing)                            | -     | 100                 | 80                  | 140                 | 120                 | -    | -    |

|                                 |                  |               |                     |                     |                     |                     |                 |                 |
|---------------------------------|------------------|---------------|---------------------|---------------------|---------------------|---------------------|-----------------|-----------------|
|                                 | $[(X_T)/(BM_h)]$ | ( $\beta_3$ ) | 0.40                | 0.32                | 0.56                | 0.48                | -               | -               |
| Short circuit evaluation result |                  |               | Not short-circuited | Not short-circuited | Not short-circuited | Not short-circuited | Short-circuited | Short-circuited |

[0230]

Table 1 reveals the following.

In Examples 1 to 4, it is revealed that a short circuit of bumps can be prevented  
5 despite the use of the semiconductor wafer having fine-pitched bumps.

On the other hand, as in Comparative Examples 1 and 2, it is also revealed that a short circuit of bumps of the semiconductor wafer having fine-pitched bumps cannot be prevented when the protective film (X) is not provided.

#### Reference Signs List

10 [0231]

1, 1a, 1b, 1c: Sheet for forming protective film

x: Curable resin film

x1: Thermosetting resin film

x2: Energy ray-curable resin film

15 X: Protection film

Y: Support sheet

11: Substrate

21: Pressure sensitive adhesive (PSA) layer

31: Intermediate layer

20 40: Semiconductor wafer with bumps

41: Semiconductor wafer

41a: Bump-formed surface

BM: Bump

CP: Semiconductor chip with protective film

Z: Wiring board

Z1: Wiring

## CLAIMS

### [Claim 1]

A sheet for forming a protective film, the sheet comprising a laminated structure of a curable resin film (x) and a support sheet (Y), wherein

5 the curable resin film (x) is a thermosetting resin film (x1) containing the polymer component (A) including poly(vinyl acetal)s, and containing thermosetting component including epoxy resin (B1), and wherein

the sheet for forming a protective film is to be used to form a protective film (X) on a bump-formed surface of a semiconductor wafer, the semiconductor wafer including  
10 a plurality of bumps and satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ):

- Requirement ( $\alpha 1$ ): A width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to 350  $\mu m$ ; and

- Requirement ( $\alpha 2$ ): A pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I):

15  $[(BM_p)/(BM_w)] \leq 1.0$  (I); and

the sheet for forming a protective film satisfies Requirements ( $\beta 1$ ) to ( $\beta 3$ ):

- Requirement ( $\beta 1$ ): A modulus of elasticity in tension at 23°C,  $E'$  (23°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^7$  Pa to  $1 \times 10^{10}$  Pa;

20 • Requirement ( $\beta 2$ ): A modulus of elasticity in tension at 260°C,  $E'$  (260°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^5$  Pa to  $1 \times 10^8$  Pa; and

- Requirement ( $\beta 3$ ): A thickness ( $X_T$ ) (unit:  $\mu m$ ) at 23°C of the protective film (X) formed by curing the curable resin film (x) and a height ( $BM_h$ ) (unit:  $\mu m$ ) of the  
25 bump satisfy Relationship (II):

$$[(X_T)/(BM_h)] \geq 0.2 \quad (II).$$

[Claim 2]

A sheet for forming a protective film, the sheet comprising a laminated structure of a curable resin film (x) and a support sheet (Y), wherein

5 the sheet for forming a protective film is to be used to form a protective film (X) on a bump-formed surface of a semiconductor wafer, the semiconductor wafer including a plurality of bumps and satisfying Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ):

- Requirement ( $\alpha 1$ ): A width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to 350  $\mu m$ ; and

10 • Requirement ( $\alpha 2$ ): A pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I):

$$[(BM_p)/(BM_w)] \leq 0.70 \quad (I); \text{ and}$$

the sheet for forming a protective film satisfies Requirements ( $\beta 1$ ) to ( $\beta 3$ ):

- Requirement ( $\beta 1$ ): A modulus of elasticity in tension at 23°C,  $E'$  (23°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^7$  Pa to  $1 \times 10^{10}$  Pa;

- Requirement ( $\beta 2$ ): A modulus of elasticity in tension at 260°C,  $E'$  (260°C), of the protective film (X) formed by curing the curable resin film (x) is from  $1 \times 10^5$  Pa to  $1 \times 10^8$  Pa; and

20 • Requirement ( $\beta 3$ ): A thickness ( $X_T$ ) (unit:  $\mu m$ ) at 23°C of the protective film (X) formed by curing the curable resin film (x) and a height ( $BM_h$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (II):

$$[(X_T)/(BM_h)] \geq 0.2 \quad (II).$$

[Claim 3]

The sheet for forming a protective film according to claim 1 or 2, the sheet further satisfying Requirement ( $\alpha 3b$ ):

• Requirement ( $\alpha 3b$ ): The height ( $BM_h$ ) of the bump and the width ( $BM_w$ ) of the bump satisfy Relationship (IIIb):

5                     $0.5 \leq [(BM_h)/(BM_w)] \leq 5.0$             (IIIb).

[Claim 4]

The sheet for forming a protective film according to any one of claims 1 to 3, the sheet further satisfying Requirement ( $\alpha 4$ ):

• Requirement ( $\alpha 4$ ): The height ( $BM_h$ ) of the bump is from 15  $\mu m$  to 300  $\mu m$ .

10    [Claim 5]

The sheet for forming a protective film according to any one of claims 1 to 4, wherein the support sheet (Y) is a back grinding tape.

[Claim 6]

A method of manufacturing a semiconductor wafer with a protective film, the  
15    method comprising:

(S1) preparing a semiconductor wafer including a bump-formed surface provided with a plurality of bumps;

(S2) bonding the sheet for forming a protective film described in any one of claims 1 to 5 to the bump-formed surface of the semiconductor wafer with pressing the  
20    sheet to the bump-formed surface of the semiconductor wafer, using the curable resin film (x) as a bonding surface; and

(S3) curing the curable resin film (x) to form the protective film (X), wherein the curable resin film (x) is a thermosetting resin film (x1) containing the polymer component (A) including poly(vinyl acetal)s, and containing thermosetting  
25    component including epoxy resin (B1) ,

and wherein the semiconductor wafer prepared in the step (S1) satisfies

Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ):

• Requirement ( $\alpha 1$ ): The width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to 350  $\mu m$ ; and

5 • Requirement ( $\alpha 2$ ): The pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I):

$$[(BM_p)/(BM_w)] \leq 1.0 \quad (I).$$

[Claim 7]

A method of manufacturing a semiconductor wafer with a protective film, the  
10 method comprising:

(S1) preparing a semiconductor wafer including a bump-formed surface provided with a plurality of bumps;

(S2) bonding the sheet for forming a protective film described in any one of claims 1 to 5 to the bump-formed surface of the semiconductor wafer with pressing the  
15 sheet to the bump-formed surface of the semiconductor wafer, using the curable resin film (x) as a bonding surface; and

(S3) curing the curable resin film (x) to form the protective film (X),

wherein the semiconductor wafer prepared in the step (S1) satisfies

Requirements ( $\alpha 1$ ) and ( $\alpha 2$ ):

20 • Requirement ( $\alpha 1$ ): The width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump is from 20  $\mu m$  to 350  $\mu m$ ; and

• Requirement ( $\alpha 2$ ): The pitch ( $BM_p$ ) (unit:  $\mu m$ ) of the bumps and the width ( $BM_w$ ) (unit:  $\mu m$ ) of the bump satisfy Relationship (I):

$$[(BM_p)/(BM_w)] \leq 0.70 \quad (I).$$

25

[Claim 8]

A method of manufacturing a semiconductor chip with a protective film, the method comprising:

5 (T1) performing the manufacturing method described in claim 6 or 7 to produce a semiconductor wafer with a protective film; and

(T2) dividing the semiconductor wafer with a protective film into individual pieces.

[Claim 9]

10 A method of manufacturing a semiconductor package, the method comprising:

(U1) performing the manufacturing method described in claim 8 to produce a semiconductor chip with a protective film; and

(U2) electrically connecting a wiring board and the semiconductor chip with a protective film via the bumps.

15 [Claim 10]

The method of manufacturing a semiconductor package according to claim 9, the method further comprising:

(U3) filling an underfill material between the wiring board and the semiconductor chip with a protective film.

20