

ADHESIVE SHEET FOR PRODUCING SEMICONDUCTOR DEVICE,
SEMICONDUCTOR DEVICE, AND PRODUCTION METHOD FOR
SEMICONDUCTOR DEVICE

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an adhesive sheet which is detachably attached to a lead frame or a wiring substrate and which is used for producing a semiconductor device, a semiconductor device comprising the adhesive sheet, and a production method for the
10 semiconductor device.

Priority is claimed on Japanese Patent Application No. 2005-099481, filed March 30, 2005, and Japanese Patent Applications Nos. 2005-316560 and 2005-316561, filed October 31, 2005, the content of which is incorporated herein by reference.

15 Description of the Related Art

Recently, with the reduction in size of electronics, such as portable personal computers and portable telephones, and increasing functions thereof, it has been desired to reduce the size of electronic elements comprising electronics, so as to integrate in high density. That is, a technique for mounting electronic elements in high density has been
20 required. In light of the above, instead of peripheral-mounting type semiconductor devices in which external terminals are mounted at a peripheral area of semiconductor devices, such as QFPs (Quad Flat Packages) and SOPs (Small Out Line Packages), surface-mounting type semiconductor devices in which external terminals are mounted on a surface of semiconductor devices in high density, such as CSPs (Chip Scale Packages)
25 have received much attention. In particular, among CSPs, since QFNs (Quad Flat

Non-leaded Packages) can be manufactured by conventional techniques, this is suitable. Therefore, QFNs have been used as low number terminal type semiconductor devices generally comprising 100 pins or fewer.

The following method has been used as a method for manufacturing QFNs.

5 First, in an adhesive sheet attaching step, an adhesive sheet is attached on one surface of a lead frame. Then, in a die attaching step, at a plurality of semiconductor element mounting parts (die pad parts), which are formed on the lead frame, semiconductor elements, such as IC chips, are mounted. In a wire bonding step, a plurality of leads, which are arranged around the semiconductor element mounting parts of the lead frame, and the semiconductor elements are electrically connected with bonding wires. Next, in a resin sealing step, the semiconductor elements are sealed with a sealing resin. After this step, in an adhesive sheet peeling step, a QFN unit, in which a plurality of QFNs are arranged, is prepared by peeling the adhesive sheet from the lead frame. In a dicing step, which is the last step, a plurality of QFNs is prepared simultaneously by dicing the prepared QFN unit along the outer edges of the QFNs.

Japanese Patent Application, First Publication No. 2002-184801 discloses an adhesive sheet comprising a silicone adhesive used in producing a QFN. Japanese Patent Application, First Publication No. 2000-294579 also discloses an adhesive sheet comprising a silicone adhesive or an acrylic adhesive used in producing a QFN.

20 However, when an adhesive sheet comprising a silicone adhesive is used, mold flash may occur due to the adhesive by itself. In addition, an out gas component may be generated from the adhesive by heating. The out gas component may adhere to the surface of lead frame and causes joint defects between the lead frame and bonding wires, or may decrease adhesiveness between the lead frame and a sealing resin. Thereby, the yielding or reliability of semiconductor devices may decrease.

Japanese Patent Application, First Publication No. 2003-33601 discloses an adhesive tape comprising a thermosetting adhesive in order to solve the problem.

On the other hand, wire bonding properties are generally more improved by removing impurities adhered on the surface of the adhesive sheet by plasma-cleaning
5 before a wire bonding step.

However, when the conventional adhesive sheet comprising a thermosetting adhesive is subjected to plasma-cleaning, an exposed surface of the adhesive sheet is roughened. Then, when the adhesive sheet is peeled, the adhesive may transfer to
(connecting terminals or a surface of the sealing resin (below, this is called "adhesive
10 transfer"). When adhesive transfer generates, the adhesive adheres to portions where the sealing resin is sealed, or external connecting terminals around the portions, and there is a possibility that connection defects generate in the resulting semiconductor device.

SUMMARY OF THE INVENTION

15 In consideration of the above described problems with conventional technology, an object of the present invention is to provide an adhesive sheet for producing a semiconductor device, which can prevent the generation of an out gas component and
(adhesive transfer while maintaining excellent wire bonding properties and mold flash properties of a thermosetting adhesive which is used in semiconductor devices such as
20 QFNs, and can thereby prevent the production of defective semiconductor devices; a semiconductor device comprising the adhesive sheet; and a production method for the semiconductor device.

In addition, another object of the present invention is to provide an adhesive sheet for producing a semiconductor device which has excellent wire bonding properties
25 without plasma-cleaning before a wire bonding step, and excellent adhesiveness between

lead frames and a sealing resin, and which provides a semiconductor device having high reliability.

In order to achieve the object, the present invention provides a first adhesive sheet for producing a semiconductor device which is detachably attached to a lead frame or a wiring substrate, wherein the adhesive sheet comprises a substrate and an adhesive layer, and the adhesive layer comprises a thermosetting resin component (a), a thermoplastic resin component (b), and a fluorine based additive (c).

It is preferable that the fluorine based additive (c) be at least one selected from the group consisting of fluorine containing graft polymers, fluorine containing block copolymers, and fluorine containing aliphatic polymer esters.

In addition, in order to achieve the object, the present invention provides a second adhesive sheet for producing a semiconductor device which is detachably attached to a lead frame or a wiring substrate, wherein the adhesive sheet comprises a substrate and an adhesive layer, and the adhesive layer comprises fluorine resin.

It is preferable that the adhesive layer comprise a thermosetting resin component (a1) and a thermoplastic resin component (b1) and that at least one of the thermosetting resin component (a1) and the thermoplastic resin component (b1) be a fluorine containing olefin resin.

It is preferable that a mass ratio ((a1)/(b1)) between the thermosetting resin component (a1) and the thermoplastic resin component (b1) be in a range from 0.05 to 0.43.

It is preferable that a mass average molecular weight of the thermoplastic resin component (b1) be in a range from 2,000 to 1,000,000.

It is preferable that a storage modulus of the adhesive layer after hardening be 0.1 MPa or greater in a temperature range from 150 to 250°C.

It is preferable that adhesive strength of the adhesive layer after hardening be in a range from 0.03 to 5 N/cm in a temperature range from 150 to 250°C.

It is preferable that the substrate be a heat resistant film having a glass transition temperature of 150°C or greater and a thermal expansion coefficient in a range from 5 to 50 ppm/°C.

It is also preferable that the substrate be a metal foil having a thermal expansion coefficient in a range from 5 to 50 ppm/°C.

In addition, in order to achieve the object, the present invention provides a third adhesive sheet for producing a semiconductor device which is detachably attached to a lead frame or a wiring substrate, wherein the adhesive sheet comprises a substrate and an adhesive layer, and the adhesive layer comprises fluorine resin and a reactive elastomer.

It is preferable that the fluorine resin be one of copolymers obtained by polymerizing a monomer material containing fluoroolefins and vinyl ethers and copolymers obtained by polymerizing a monomer material containing fluoroolefins and vinyl esters.

It is preferable that the reactive elastomer be a maleic anhydride containing styrene-ethylene-butylene copolymer.

It is also preferable that a protective film be provided on one surface of the adhesive layer.

In addition, in order to achieve the object, the present invention provides a semiconductor device produced using one of the first to third adhesive sheets for producing a semiconductor device.

Furthermore, in order to achieve the object, the present invention provide a production method for a semiconductor device comprising one of the first to third adhesive sheets for producing a semiconductor device.

In the description and claims, "fluoroolefins" means olefins of which hydrogen is partially or entirely substituted with a fluorine atom. Specifically, "fluoroolefins" contains olefins of which hydrogen is partially or entirely substituted with a fluorine atom and olefins of which hydrogen is partially substituted with a fluorine atom and the remaining hydrogen is partially or entirely substituted with other atoms such as a chlorine atom. In addition, "fluorine resin" means fluorine containing resins.

In general, in a resin sealing step in producing a semiconductor device, the semiconductor device is sealed with resin under pressure of 5 to 10 GPa while heating to 150 to 200°C. As a result of subjecting the adhesive layer of the adhesive sheet to high temperatures, adhesive strength of the adhesive layer (adhesiveness between the adhesive layer and the lead frame) decreases, then the adhesive layer is partially peeled from the lead frame due to pressure of the sealing resin, and mold flash may occur. However, according to the adhesive sheets of the present invention, adhesive strength of the adhesive layer does not decrease, and such problems do not occur.

In the present invention, it is possible to prevent the generation of out gas components which occurs in a silicone adhesive. In addition, it is also possible to prevent the occurrence of adhesive transfer while maintaining excellent wire bonding properties and mold flash properties of thermosetting adhesives when the adhesive sheet comprising a thermosetting adhesive resin is used in semiconductor devices, and can thereby prevent the production of defective semiconductor devices.

In addition, it is possible to provide an adhesive sheet for producing a semiconductor device which has excellent wire bonding properties even when the adhesive sheet is not subjected to a plasma-cleaning before a wire bonding step, and excellent adhesiveness between the lead frame and the sealing resin, and which provides semiconductor devices having high reliability.

Furthermore, it is also possible to provide an adhesive sheet for producing a semiconductor device which has preferable peeling properties and does not cause adhesive transfer even when the adhesive layer of the adhesive sheet is subjected to a plasma-cleaning before a wire bonding step.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plane view showing a lead frame which is suitably used for producing QFNs using the adhesive sheet of the present invention.

(FIGS. 2A to 2F show steps for producing QFNs using the adhesive sheet of the
10 present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Below, the adhesive sheet for producing a semiconductor device, the semiconductor device, and the production method for the semiconductor device of the
15 present invention will be explained in detailed.

The adhesive sheet for producing a semiconductor device of the present invention is detachably attached to a lead frame or a wiring substrate. Here, "a lead frame" is a
(conductive pattern element obtained by etching or pressing a metal plate, and "a wire
substrate" is an element obtained by forming and adhere the conductive pattern element
20 made of conductive material on (or sometimes inside) the surface of an electric insulating
substrate.

In the following, for descriptive purpose, the adhesive sheet of the present invention is explained by using the lead frame as an adhered subject; however, of course, the adhesive sheet of the present invention can also applied to the wire substrate.

25 The adhesive sheet of the present invention comprises a substrate and an adhesive

layer.

Examples of the substrate include heat resistant material such as heat resistant films, and metal foils.

When semiconductor devices, such as QFNs are produced using the adhesive sheet of the present invention, the adhesive sheet is subjected to high temperatures such as 150 to 250°C, in a die attaching step, a wire bonding step, and a resin sealing step. When a heat resistant film is used for the substrate and the heat resistant film is heated to the glass transition temperature (T_g) thereof or greater, the thermal expansion coefficient of the heat resistant film increases suddenly. Thereby, the volume difference between the metal lead frame and the heat resistant film increases. As a result, when the lead frame and the heat resistant film are cooled to room temperature, there is a possibility that warps are caused in the lead frame and the heat resistant film. When warps are generated in the lead frame and the heat resistant film, in a resin sealing step, it is impossible to mount the lead frame on positioning pins comprising a die, and there is a possibility that dislocation will occur.

Therefore, when a heat resistant film is used for the substrate, the glass transition temperature of the heat resistant film is preferably 150°C or greater, and more preferably 180°C or greater.

In addition, the thermal expansion coefficient at 150 to 250°C of the heat resistant film is preferably 5 to 50 ppm/°C, and more preferably 10 to 30 ppm/°C. The heat resistant film includes, for example, films made of polyimides, polyamides, polyether sulfones, polyphenylene sulfides, polyether ketones, polyether ether ketones, triacetyl cellulose, and polyetherimides.

Moreover, when a metal foil is used for the substrate, for the same reasons in the heat resistant film, the thermal expansion coefficient at 150 to 250°C of the metal foil is

preferably 5 to 50 ppm/°C, and more preferably 10 to 30 ppm/°C. The metal foil includes, for example, foils made of gold, silver, copper, platinum, aluminum, magnesium, titanium, chromium, manganese, iron, cobalt, nickel, zinc, palladium, cadmium, indium, tin, and lead; foils containing alloys thereof as a main component, and foils plated thereby.

5 In order to prevent the occurrence of adhesive transfer in an adhesive sheet peeling step in producing the semiconductor using the adhesive sheet, when S_a is adhesive strength between the substrate and the adhesive layer, and S_b is adhesive strength between the sealing resin and lead frame and the adhesive layer, an adhesive strength ratio, S_a/S_b , is preferably 1.5 or greater. When S_a/S_b is 1.5 or greater, adhesive transfer is not easily
10 generated in the adhesive sheet peeling step. In order to make the adhesive strength ratio, S_a/S_b , 1.5 or greater, when the heat resistant film is used for the substrate, before forming the adhesive layer, it is preferable that a surface of the heat resistant film, at which the adhesive layer will be formed, to be treated such that the adhesive strength S_a is increased, such as a corona treatment, a plasma treatment, a primer treatment, and a sand blast
15 treatment. Moreover, metal foils are classified into rolled metal foils and electrolytic metal foils, depending on the production method thereof. In order to make the adhesive strength ratio, S_a/S_b , 1.5 or greater, it is preferable to use an electrolytic metal foil, and to form the adhesive layer on a rough surface of the electrolytic metal foil. Among the electrolytic metal foils, an electrolytic copper foil is most preferable.

20 In order to prevent the occurrence of mold flash, it is preferable that adhesive strength to the lead frame of the adhesive layer in a range of 150 to 200 °C after hardening be in a range from 0.03 to 5 N/cm. When it is 0.03 N/cm or greater, mold flash does not easily occur, and when it is 5 N/cm or less, adhesive transfer does not easily occur.

For producing, it is preferable that adhesive strength of the adhesive sheet to the
25 lead frame at room temperature before hardening be 0.98 N/cm or greater. When it is

0.98 N/cm or greater, the adhesive layer does not readily peel from the lead frame during transportation in producing. The measurement method for adhesive strength will be explained in the following Examples.

Below, the first adhesive sheet for producing a semiconductor device of the present invention will be explained in detailed.

The adhesive layer of the first adhesive sheet for producing a semiconductor device comprises a thermosetting resin component (a) and a thermoplastic resin component (b), which are a base of the adhesive, that is, main components or matrix, and further comprises a fluorine based additive (c). In other words, the adhesive layer comprises essentially the fluorine based additive (c), and further comprises the thermosetting resin component (a) and the thermoplastic resin component (b), of which kinds (chemical structure, molecular weight, and the like) are different from those of the fluorine based additive (c). The adhesive layer always comprises three components or greater.

The total amount of the thermosetting resin component (a) and the thermoplastic resin component (b) is preferably 95 parts by mass, and more preferably 97 to 99.9 parts by mass relative to 100 parts by mass of the adhesive layer. When it is 95 parts by mass or greater, functions as an adhesive layer are sufficiently obtained.

A mass ratio ((a)/(b)) between the thermosetting resin component (a) and the thermoplastic resin component (b) is preferably in a range from 0.05 to 2, and more preferably in a range from 0.3 to 1.6. When it is in the range, since the balance between the thermosetting resin component (a) and the thermoplastic resin component (b) is good, and separation in the components is more improved and cohesion of the adhesive layer is also improved.

The thermosetting resin component (a) and/or the thermoplastic resin component

(b) may contain fluorine resin. In this case, when (a)/(b) is 2 or less, a component containing fluorine and a component not containing fluorine do not separate in producing a coating, and the adhesive layer is produced easily. When it is 0.05 or greater, cohesion of the adhesive layer does not decrease, and the occurrence of mold flash is more prevented during a resin sealing step.

Thermosetting resin component (a)

Examples of the thermosetting resin component (a) include urea resins, melamine resins, benzoguanamine resins, acetoguanamine resins, phenol resins, resorcinol resins, xylene resins, furan resins, unsaturated polyester resins, diallylic phthalate resins, isocyanate resins, epoxy resins, maleimide resins, and nadimide resins. These thermosetting resins can be used alone or in combinations of two or more.

Among these thermosetting resins, when at least one of epoxy resins and phenol resins is contained as the thermosetting component (a), the adhesive layer has a high elastic modulus at a treatment temperature in the wire bonding step, and an excellent adhesive strength to the lead frame at a treatment temperature in a resin sealing step.

Fluorine resin may be used as the thermosetting resin component (a). Fluorine resin used as the thermosetting resin component (a) is different from the essential fluorine based additive (c) in a chemical structure and a use amount.

Examples of the fluorine resin which is used as the thermosetting resin component (a) include fluorine containing thermosetting resins such as urea resins, melamine resins, benzoguanamine resins, acetoguanamine resins, phenol resins, resorcinol resins, xylene resins, furan resins, unsaturated polyester resins, diallylic phthalate resins, isocyanate resins, epoxy resins, maleimide resins, and nadimide resins; copolymers obtained by copolymerizing olefin resins such as vinylidene difluoride,

hexafluoropropylene, tetrafluoroethylene, and perfluoromethyl vinyl ether with a monomer containing a functional group (reactive group); and copolymers obtained by copolymerizing two or more kinds of these monomers. Copolymers obtained by further copolymerizing ethylene, propylene, or alkyl vinyl ethers with the polymer or copolymer are also used. Among these fluorine containing thermosetting resins, fluorine containing olefin resins having a functional group are preferable, because they contain many fluorine atoms, and have high resistance to plasma-cleaning before a wire bonding step.

More specific examples thereof include the fluorine resin which is one of copolymers obtained by copolymerizing a monomer material containing fluoroolefins and hydrocarbon based monomers such as vinyl ethers and vinyl esters and which has a functional group such as a hydroxyl group, a carboxyl group, and an epoxy group.

The fluorine resin containing a functional group are produced by adding a monomer containing a functional group in the monomer material and copolymerizing them. It is also possible to produce fluorine resin containing a functional group by producing fluorine resin containing a unsaturated bond such as a vinyl group and then introducing a functional group such as an epoxy group in the unsaturated bond.

Examples of the monomer containing a functional group include monomers containing a vinyl bond and a functional group, such as an acrylic acid monomer and a methacrylic acid monomer. Such fluorine resin is commercialized.

Among these, copolymers obtained by copolymerizing a monomer material containing fluoroolefins and vinyl ethers and/or copolymers obtained by copolymerizing a monomer material containing fluoroolefins and vinyl esters, and which have a functional group such as a hydroxyl group, a carboxyl group, and an epoxy group, are preferable, because the adhesive layer comprising the copolymer can prevent mold resin leakage and be peeled without occurring adhesive transfer.

More preferable examples thereof include:

resins having a functional group and being copolymers obtained by copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of cyclohexylvinyl ethers, alkyl vinyl ethers, and hydroxyalkyl vinyl ethers;

5 resins having a functional group and being copolymers obtained by copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of alkyl vinyl ethers, and allyl alcohols; and

resins having a functional group and being copolymers obtained by copolymerizing trifluoroethylene with at least one monomer selected from the group
(consisting of aliphatic carboxylic vinyl esters, and hydroxyalkyl vinyl esters.
10

Examples of such commercialized fluorine resin include a fluoroethylene vinyl ether copolymer (trade name: LUMIFLON ®; marketed by ASAHI GLASS COMPANY; having a hydroxyl group and a carboxyl group as a functional group).

When the fluorine resin is contained as the thermosetting resin component (a), the
15 amount is preferably in a range from 5 to 40 parts by mass, and more preferably in a range from 20 to 30 parts by mass, relative to 100 parts by mass of the adhesive layer. When it is 5 parts by mass or greater, peeling properties are excellent, and it is possible to prevent
(more certainly the occurrence of adhesive transfer. When it is 40 parts by mass or less, compatibility to other resin components is more improved, and it is effective in producing.

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Thermoplastic resin component (b)

Examples of the thermoplastic resin component (b) include acrylonitrile-butadiene copolymers (NBR), acrylonitrile-butadiene-styrene resins (ABS), styrene-butadiene-ethylene resins (SEBS), styrene-butadiene-styrene resins (SBS),
25 polybutadienes, polyacrylonitriles, polyvinyl butyrals, polyamides, polyamideimides,

polyimides, polyesters, polyurethanes, and acrylic rubbers. These thermoplastic resins can be used alone or in combinations of two or more.

Fluorine resin may be added to the thermoplastic resin component (b).

Examples of the fluorine resin, which is added to the thermoplastic resin component (b),

5 include fluorine containing thermoplastic resins such as an acrylonitrile-butadiene copolymers (NBR), acrylonitrile-butadiene-styrene resins (ABS), styrene-butadiene-ethylene resins (SEBS), styrene-butadiene-styrene resins (SBS), styrene-ethylene-butylene resins, polybutadienes, polyacrylonitriles, polyvinyl butyrals, (polyamides, polyamideimides, polyimides, polyesters, polyurethanes, and acrylic rubbers; 10 polymers obtained by polymerizing olefin resins such as vinylidene difluoride, hexafluoropropylene, tetrafluoroethylene, and perfluoromethyl vinyl ether; and copolymers obtained by copolymerizing two or more kinds of the monomers.

Copolymers obtained by further copolymerizing ethylene, propylene, or alkyl vinyl ethers with the polymer or the copolymer are also used. Among these fluorine containing

15 thermosetting resins, fluorine containing olefin resins are preferable because they contain many fluorine atoms, and have high resistance to plasma-cleaning before a wire bonding step.

More specific examples thereof include copolymers obtained by copolymerizing a monomer material containing fluoroolefins and hydrocarbon based monomers such as 20 vinyl ethers, and vinyl esters.

Among these, copolymers obtained by copolymerizing a monomer material containing fluoroolefins and vinyl ethers and/or copolymers obtained by copolymerizing a monomer material containing fluoroolefins and vinyl esters are preferable, because the adhesive layer comprising the copolymer can prevent mold resin leakage and be peeled 25 without occurring adhesive transfer.

More preferable examples thereof include:

copolymers obtained by copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of cyclohexylvinyl ethers, alkyl vinyl ethers, and hydroxyalkyl vinyl ethers;

5 copolymers obtained by copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of alkyl vinyl ethers, and allyl alcohols; and

 copolymers obtained by copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of aliphatic carboxylic vinyl esters and
(hydroxyalkyl vinyl esters.

10 When the fluorine resin is contained in the thermoplastic resin component (b), the amount is preferably in a range from 5 to 40 parts by mass, and more preferably in a range from 20 to 30 parts by mass, relative to 100 parts by mass of the adhesive layer. When it is 5 parts by mass or greater, peeling properties are excellent, and it is possible to prevent more certainly the occurrence of adhesive transfer. When it is 40 parts by mass or less,
15 compatibility to other resin components is more improved, and it is effective in producing.

 The effects of the present invention are easily obtained by adding a reactive elastomer in the thermoplastic resin component (b).
(

 Examples of the reactive elastomer include elastic resin which has reactivity due to having a structural unit derived from a functional group such as a carboxyl group, an
20 amino group, a vinyl group, and an epoxy group, and acid anhydride monomers such as maleic anhydride.

 The reactive elastomer is produced by copolymerizing monomers having a functional group or acid anhydride monomers in producing the elastic resin. It is also possible to produce the reactive elastomer by producing elastic resins having an
25 unsaturated bond such as a vinyl bond, and then introducing a functional group such as an

epoxy group in the unsaturated bond. Examples of the monomers containing a functional group include monomers having a vinyl bond and a functional group, such as an acrylic acid monomer and a methacrylic acid monomer.

Specific examples thereof include a carboxyl group containing styrene-butadiene copolymers, a carboxyl group containing styrene-isoprene copolymers, a carboxyl group containing styrene-butadiene saturated copolymers, a carboxyl group containing styrene-isoprene saturated copolymers, a carboxyl group containing styrene-ethylene-butene-styrene copolymers, a carboxyl group containing styrene-ethylene-butene-styrene saturated copolymers, a carboxyl group containing acrylonitrile-butadiene copolymers, an amino group modified polyol resins, an amino group modified phenoxy resins, an amino group modified acrylonitrile-butadiene copolymers, polyvinylbutyral resins, polyvinylacetal resins, a carboxyl group containing acrylonitrile-butadiene copolymers, a hydrogenated carboxyl group containing acrylonitrile-butadiene copolymers, a carboxyl group containing acrylic rubbers, maleic anhydride containing styrene-butadiene copolymers, maleic anhydride containing styrene-ethylene-butene-styrene copolymers, a hydroxyl group end saturated copolymer polyester resins, a carboxyl group end saturated copolymer polyester resins, an epoxy group containing styrene based block copolymers, and maleic anhydride containing styrene-ethylene-butylene copolymers. These reactive elastomers can be used alone or in combinations of two or more. "Maleic anhydride containing" means "copolymerized with maleic anhydride".

Among these, for example, the followings are commercialized.

As a carboxyl group containing acrylonitrile-butadiene copolymer:

trade name: NIPOL ® 1072J, marketed by ZEON CORPORATION

trade name: NIPOL ® DN631, marketed by ZEON CORPORATION

trade name: HYCAR ® CTBN, marketed by Ube Industries Ltd.

trade name: PNR-1H, marketed by JSR Corporation

As an amino group containing acrylonitrile-butadiene copolymer:

trade name: HYCAR ® ATBN, marketed by Ube Industries Ltd.

5 As a maleic anhydride containing styrene-ethylene-butylene copolymer:

trade name: TUFTECH ® M-series marketed by Asahi Kasei Chemicals Corporation

As an epoxy group containing styrene based block copolymer:

(trade name: EPOFRIEND®, marketed by Daicel Chemical Industries, Ltd.

10 Among these, a maleic anhydride containing styrene-ethylene-butylene copolymer is preferable, because the adhesive layer comprising the copolymer can prevent mold resin leakage and be peeled without occurring adhesive transfer. In the copolymer, it is preferable that a mass ratio between maleic anhydride: styrene: ethylene-butylene (total mass of ethylene and butylene) be preferably 0.3 to 3: 10 to 40: 60 to 90, and more
15 preferably 0.5 to 1: 20 to 30: 70 to 80.

The content of the reactive elastomer is preferably 30 to 95 parts by mass, and more preferably 40 to 90 parts by mass, relative to 100 parts by mass of the adhesive layer.

(When it is 30 parts by mass or greater, it is possible to prevent more certainly the occurrence of mold flash and adhesive transfer. When it is 95 parts by mass or less,
20 peeling properties are improved and adhesive transfer is more prevented.

The mass average molecular weight of the thermoplastic resin component (b) is preferably 2,000 to 1,000,000, more preferably 5,000 to 800,000, and most preferably 10,000 to 500,000. The thermoplastic resin component (b) having such a mass average molecular weight increases cohesion of the adhesive layer, and this can thereby prevent
25 the generation of adhesive transfer in the adhesive sheet peeling step.

Fluorine based additive (c)

The fluorine based additive (c) is preferably resin (also may be an oligomer).

Examples of the fluorine based additive (c) include fluorine containing graft polymers,

5 fluorine containing block copolymers, and fluorine containing aliphatic polymer esters.

These fluorine based additives can be used alone or in combinations of two or more. The resin used for the fluorine based additive (c) is preferably thermoplastic resin.

Examples of the fluorine containing graft polymer include a fluorine containing
(acrylic graft polymer (trade name: CHEMTREE ® LF-700, marketed by Soken Chemical
10 & Engineering Co. Ltd). "A fluorine containing acrylic graft polymer" is a polymer
comprising an acrylic main polymer and plural branched fluorine containing polymers.

Examples of the fluorine containing block copolymer include a block copolymer
comprising a fluorinated alkyl group containing polymeric segment and an acrylic
polymeric segment (trade name: MODIPER® F-series, for example, MODIPER® F-200,
15 MODIPER ® F-220, MODIPER ® F-2020, MODIPER ® F-3035, and MODIPER ®
F-600, marketed by NOF Corporation).

(Fluorine aliphatic polymer esters have preferably characteristics of a nonionic
surfactant, and Examples thereof include trade name of NOVEC® F-4430, marketed by
3M.

20 Among these, a fluorine containing graft polymer or a fluorine containing block
copolymer is preferable, because the adhesive layer comprising it can prevent mold resin
leakage and be peeled without occurring adhesive transfer.

The content of the fluorine base additive (c) is preferably 0.1 to 5 parts by mass,
and more preferably 0.5 to 3 parts by mass, relative to 100 parts by mass of the adhesive
25 layer. When it is 0.1 parts by mass or greater, the effects of the present invention are

easily obtained. From the viewpoint of balance among materials comprising a base material of the adhesive layer, effects of the present invention, and economic efficiency, it is preferable 5 parts by mass or less.

In order to adjust the thermal expansion coefficient, thermal conductivity, surface
5 tack, adhesive strength, and the like of the adhesive layer, it is preferable to add an inorganic or organic filler in the adhesive layer. The inorganic filler includes, for example, crush type silica, melt type silica, alumina, titanium oxide, beryllium oxide, magnesium oxide, calcium carbonate, titanium nitrides, silicon nitride, boron nitride,
(titanium boride, tungsten boride, silicon carbide, titanium carbide, zirconium carbide,
10 molybdenum carbide, mica, zinc oxide, carbon black, aluminum hydroxide, calcium hydroxide, magnesium hydroxide, and antimony trioxide; and fillers, which are made thereof and which have a surface having a trimethylsiloxane group and the like. The organic filler includes, for example, fillers made of polyimides, polyamideimides, polyether etherketones, polyetherimides, polyesterimides, nylons, and silicone resins.

15 Below, the second adhesive sheet for producing a semiconductor device of the present invention will be explained in detailed.

(The adhesive layer of the second adhesive sheet for producing a semiconductor device comprises fluorine resin. Here, "fluorine resin" means widely resins comprising a fluorine atom as explained above.

20 The adhesive layer preferably comprises a thermosetting resin component (a1) and a thermoplastic resin component (b1), and at least one of the thermosetting resin component (a1) and the thermoplastic resin component (b1) comprises preferably a fluorine resin. In this case, a mass ratio ((a1)/(b1)) between the thermosetting resin component (a1) and the thermoplastic resin component (b1) is preferably in a range from
25 0.05 to 0.43, and more preferably in a range from 0.11 to 0.25.

When the mass ratio ((a1)/(b1)) is 0.43 or less, since a resin component containing fluorine and a resin component not containing fluorine do not separate in producing a coating, and the adhesive layer is produced easily. When it is 0.05 or greater, cohesion of the adhesive layer does not decrease, and the occurrence of mold flash is more prevented during a resin sealing step.

Thermosetting resin component (a1)

Examples of the thermosetting resin component (a1) include urea resins, melamine resins, benzoguanamine resins, acetoguanamine resins, phenol resins, resorcinol resins, xylene resins, furan resins, unsaturated polyester resins, diallylic phthalate resins, isocyanate resins, epoxy resins, maleimide resins, and nadimide resins. These thermosetting resins can be used alone or in combinations of two or more.

Among these thermosetting resins, when at least one of epoxy resins and phenol resins is contained as the thermosetting component (a1), the adhesive layer has a high elastic modulus at a treatment temperature in a wire bonding step, and an excellent adhesive strength to the lead frame at a treatment temperature in a resin sealing step.

Fluorine containing thermosetting resin may be used as the thermosetting resin component (a1). Examples of the fluorine containing thermosetting resin used as the thermosetting resin component (a1) include the above-mentioned thermosetting resins in which fluorine is introduced; copolymers obtained by copolymerizing olefin resins such as vinylidene difluoride, hexafluoropropylene, tetrafluoroethylene, and perfluoromethyl vinyl ether with a monomer containing a reactive functional group; and copolymers obtained by copolymerizing two or more kinds of these monomers. Copolymers obtained by further copolymerizing ethylene, propylene, or alkyl vinyl ethers with the polymer or copolymer are also used. Among these fluorine containing thermosetting resins, fluorine containing

olefin resins are preferable because they contain many fluorine atoms, and have high resistance to plasma-cleaning before a wire bonding step.

Thermoplastic resin component (b1)

5 Examples of the thermoplastic resin component (b1) include acrylonitrile-butadiene copolymers (NBR), acrylonitrile-butadiene-styrene resins (ABS), styrene-butadiene-ethylene resins (SEBS), styrene-butadiene-styrene resins (SBS), polybutadienes, polyacrylonitriles, polyvinyl butyrals, polyamides, polyamideimides, polyimides, polyesters, polyurethanes, and acrylic rubbers. These thermoplastic resins
(can be used alone or in combinations of two or more.

Fluorine containing thermoplastic resin may be used as the thermoplastic resin component (b1). Examples of the fluorine containing thermoplastic resin used as the thermoplastic resin component (b1) include the above-mentioned thermoplastic resins in which a fluorine is introduced; polymers obtained by polymerizing olefin resins such as
15 vinylidene difluoride, hexafluoropropylene, tetrafluoroethylene, and perfluoromethyl vinyl ether; and copolymers obtained by copolymerizing two or more kinds of monomers. Copolymers obtained by further copolymerizing ethylene, propylene, or alkyl vinyl ethers
(with the polymer or the copolymer are also used. Among these fluorine containing thermosetting resins, fluorine containing olefin resins are preferable because they contain
20 many fluorine atoms, and have high resistance to plasma-cleaning before a wire bonding step.

A mass average molecular weight of the thermoplastic resin component (b1) is preferably 2,000 to 1,000,000, more preferably 5,000 to 800,000, and most preferably 10,000 to 500,000. The thermoplastic resin component (b1) having such a mass average
25 molecular weight improves cohesion of the adhesive layer, and this can thereby prevent

the generation of adhesive transfer in an adhesive sheet peeling step.

Similar to the adhesive layer of the first adhesive sheet, the adhesive layer of the second adhesive sheet comprises preferably an inorganic or organic filler in the adhesive layer, in order to adjust the thermal expansion coefficient, thermal conductivity, surface
5 tack, adhesive strength, and the like of the adhesive layer.

Below, the third adhesive sheet for producing a semiconductor device of the present invention will be explained in detailed.

The adhesive layer of the third adhesive sheet for producing a semiconductor
(device comprises fluorine resin and a reactive elastomer. Here, "fluorine resin" means
10 widely resins comprising a fluorine atom as explained above.

Fluorine resin

Examples of the fluorine resin include copolymers obtained by copolymerizing olefin resins such as vinylidene difluoride, hexafluoropropylene, tetrafluoroethylene, and
15 perfluoromethyl vinyl ethers with a monomer containing a functional group (reactive group); and copolymers obtained by copolymerizing two or more kinds of these monomers. Copolymers obtained by further copolymerizing ethylene, propylene, or
(alkyl vinyl ethers with the polymer or copolymer are also used. Among the fluorine resins, fluorine containing olefin resins are preferable because they contains many fluorine
20 atoms, and have high resistance to plasma-cleaning before a wire bonding step.

More specific examples thereof include fluorine resin which is copolymer obtained by copolymerizing a monomer material containing fluoroolefins and hydrocarbon based monomers such as vinyl ethers and vinyl esters and which have a functional group such as a hydroxyl group, a carboxyl group, and an epoxy group.

25 The fluorine resin containing a functional group is produced by adding a

monomer containing a functional group in the monomer material and copolymerizing them. It is also possible to produce the fluorine resin containing a functional group by producing fluorine resin containing an unsaturated bond such as a vinyl group and then introducing a functional group such as an epoxy group in the unsaturated bond.

5 Examples of the monomer containing a functional group include monomers containing a vinyl bond and a functional group, such as an acrylic acid monomer and a methacrylic acid monomer. Such fluorine resin is commercialized.

 Among the commercialized fluorine resin, copolymers obtained by
(copolymerizing a monomer material containing fluoroolefins and vinyl ethers and/or
10 copolymers obtained by copolymerizing a monomer material containing fluoroolefins and vinyl esters, and which have a functional group such as a hydroxyl group, a carboxyl group, and an epoxy group, are preferable, because the adhesive layer comprising the copolymer can prevent mold resin leakage and be peeled without occurring adhesive transfer.

15 More preferable examples thereof include:

 resins having a functional group and being copolymers obtained by
(copolymerizing trifluoroethylene with at least one monomer selected from the group
consisting of cyclohexylvinyl ether, alkyl vinyl ethers, and hydroxyalkyl vinyl ethers;

 a resin having a functional group and being copolymers obtained by
20 copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of alkyl vinyl ethers, and allyl alcohols; and

 a resin having a functional group and being copolymers obtained by
copolymerizing trifluoroethylene with at least one monomer selected from the group consisting of aliphatic carboxylic vinyl esters, and hydroxyalkyl vinyl esters.

25 Examples of such commercialized fluorine resin include a fluoroethylene vinyl

ether copolymer (trade name: LUMIFLON ®; marketed by ASAHI GLASS COMPANY; having a hydroxyl group and a carboxyl group as a functional group).

The content of the fluorine resin is preferably in a range from 5 to 40 parts by mass, and more preferably in a range from 20 to 30 parts by mass, relative to 100 parts by mass of the adhesive layer. When it is 5 parts by mass or greater, peeling properties are more improved, and it is possible to prevent more certainly the occurrence of adhesive transfer. When it is 40 parts by mass or less, compatibility to other resin components is more improved, and it is effective in producing.

10 Reactive elastomer

Examples of the reactive elastomer include elastic resin which has reactivity due to having a structural unit derived from a functional group such as a carboxyl group, an amino group, a vinyl group, and an epoxy group, and acid anhydride monomers such as maleic anhydride.

15 The reactive elastomer is produced by copolymerizing monomers having a functional group or acid anhydride monomers in producing the elastic resin. It is also possible to produce the reactive elastomer by producing elastic resin having an unsaturated bond such as a vinyl bond, and then introducing a functional group such as an epoxy group in the unsaturated bond. Examples of the monomer having a functional group include monomers having a vinyl bond and a functional group, such as an acrylic acid monomer and a methacrylic acid monomer.

Specific examples thereof include a carboxyl group containing styrene-butadiene copolymers, a carboxyl group containing styrene-isoprene copolymers, a carboxyl group containing styrene-butadiene saturated copolymers, a carboxyl group containing styrene-isoprene saturated copolymers, a carboxyl group containing

styrene-ethylene-butene-styrene copolymers, a carboxyl group containing styrene-ethylene-butene-styrene saturated copolymers, a carboxyl group containing acrylonitrile-butadiene copolymers, an amino group modified polyol resins, an amino group modified phenoxy resins, an amino group modified acrylonitrile-butadiene copolymers, polyvinylbutyral resins, polyvinylacetal resins, a carboxyl group containing acrylonitrile-butadiene copolymers, a hydrogenated carboxyl group containing acrylonitrile-butadiene copolymers, a carboxyl group containing acrylic rubbers, maleic anhydride containing styrene-butadiene copolymers, maleic anhydride containing styrene-ethylene-styrene copolymers, a hydroxyl group end saturated copolymeric polyester resins, a carboxyl group end saturated copolymeric polyester resins, an epoxy group containing styrene based block copolymers, and maleic anhydride containing styrene-ethylene-butylene copolymers. These reactive elastomers can be used alone or in combinations of two or more. "Maleic anhydride containing" means "copolymerized with maleic anhydride".

Among these, for example, the followings are commercialized.

As a carboxyl group containing acrylonitrile-butadiene copolymer:

trade name: NIPOL ® 1072J, marketed by ZEON CORPORATION

trade name: NIPOL ® DN631, marketed by ZEON CORPORATION

trade name: HYCAR ® CTBN, marketed by Ube Industries Ltd.

trade name: PNR-1H, marketed by JSR Corporation

As an amino group containing acrylonitrile-butadiene copolymer:

trade name: HYCAR ® ATBN, marketed by Ube Industries Ltd.

As a maleic anhydride containing styrene-ethylene-butylene copolymer:

trade name: TUFTECH ® M-series marketed by Asahi Kasei Chemicals

Corporation

As an epoxy group containing styrene based block copolymer:

trade name: EPOFRIEND®, marketed by Daicel Chemical Industries, Ltd.

Among these, maleic anhydride containing styrene-ethylene-butylene copolymers are preferable, because the adhesive layer comprising the copolymer can prevent mold resin leakage and be peeled without occurring adhesive transfer. In the copolymer, a mass ratio between maleic anhydride: styrene: ethylene-butylene (total mass of ethylene and butylene) is preferably 0.3 to 3: 10 to 40: 60 to 90, and more preferably 0.5 to 1: 20 to 30: 70 to 80.

The content of the reactive elastomer is preferably 30 to 95 parts by mass, and more preferably 40 to 90 parts by mass, relative to 100 parts by mass of the adhesive layer. When it is 30 parts by mass or greater, it is possible to prevent more certainly the occurrence of mold flash and adhesive transfer. When it is 95 parts by mass or less, peeling properties are improved and adhesive transfer is more prevented.

Peeling force of the adhesive sheet is more improved by adding a fluorine based additive in the adhesive layer. The fluorine based additive is preferably the fluorine based additive (c) contained in the adhesive layer of the first adhesive sheet.

The adhesive layer may contain thermosetting resin, thermoplastic resin, fluorine resin, a hardening agent cross-linkable with the reactive elastomer, and a hardening accelerator such as a dehydration catalyst. The thermosetting resin and the thermoplastic resin contained in the adhesive layer of the third adhesive sheet may be the thermosetting resin and the thermoplastic resin used in the adhesive layer of the first adhesive sheet.

Similar to the adhesive layer of the first adhesive sheet, the adhesive layer of the third adhesive sheet comprises preferably an inorganic or organic filler in the adhesive layer, in order to adjust the thermal expansion coefficient, thermal conductivity, surface tack, adhesive strength, and the like of the adhesive layer.

Then, the method for producing the adhesive layer of the first to second adhesive sheet on one surface of the substrate will be explained.

As a method for forming the adhesive layer on one surface of the substrate, for example, a casting method in which an adhesive is coated directly on the substrate and the adhesive is dried, and a lamination method in which an adhesive is coated once on a release film, the adhesive is dried and then the adhesive is transferred to the substrate, are preferable.

In addition, an organic solvent is preferably used together with the thermosetting resin component and the thermoplastic resin component. The organic solvent includes, for example, aromatic solvents such as toluene, xylene, and chlorobenzene; ketone solvents such as acetone, methylethylketone, and methylisobutylketone; aprotic polar solvents such as dimethyl formamide, dimethyl acetoamide, and N-methyl pyrrolidone; and tetrahydrofuran. These organic solvents can be used alone or in combinations of two or more. When the organic solvent is used, it is preferable to solve 1 % by mass or greater, preferably 5% by mass or greater of the mixture containing the thermosetting resin components and the thermoplastic resin components in 100% by mass of the solvent, and obtain an adhesive coating.

In particular, when the adhesive layer contains thermosetting resin component, it is preferable that the adhesive coating contain a hardening agent such as

2-ethyl-4-methylimidazole, and if necessary further contain a hardening accelerator.

In the adhesive sheet of the present invention, a release protective film may be attached on the adhesive layer of the adhesive sheet, and the protective film may be released from the adhesive layer just before production of the semiconductor devices. In this case, from the time the adhesive sheet is produced to the time it is used, the adhesive layer is protected from damage. As the protective film, any film having releasability can

be used. The protective film includes, for example, films made of polyesters, polyethylene, polypropylene, and polyethylene terephthalates; and films which are made of these polymers and of which the surface is treated with silicone resin or fluorine compounds so as to be able to release the film from the adhesive layer.

5 The storage modulus at 150 to 250°C after hardening of the adhesive layer is preferably 0.1 MPa or greater, more preferably 1 MPa or greater, and most preferably 5 MPa or greater. In the specification, "adhesive layer after hardening" means the adhesive layer which is heated in a die attaching step. In a wire bonding step for producing the semiconductor device, while the semiconductor element and the lead frame are connected
(using bonding wires, the two ends of the bonding wires are heated to 150 to 250°C and
10 melted by applying ultrasonic waves of 60 to 120 kHz. During this step, the adhesive layer of the adhesive sheet, which is positioned directly below the lead frame, is subjected to a high temperature, and the elasticity of the adhesive layer is degraded. Thereby, the adhesive layer easily absorbs the ultrasonic waves. As this result, the lead frame easily
15 vibrates, and wires bonding defects are easily generated. However, in the adhesive sheet of the present invention, which comprises the adhesive layer having an improved storage modulus, this problem is hardly generated.
(

Production method for semiconductor devices

20 Next, one production method for a semiconductor device using the adhesive sheet of the present invention will be explained referring to FIGS. 1 and 2. Below, as a semiconductor device, the QFN is exemplified. FIG. 1 is a plane view showing the lead frame viewed from the side at which the semiconductor elements are mounted. FIGS. 2A to 2F show steps for producing QFNs using the lead frame shown in FIG. 1, and this is
25 an enlarged cross-sectional view along line A-A of FIG. 1.

In order to produce QFNs, the lead frame 20 is prepared. The lead frame 20 comprises a plurality of semiconductor element mounting parts (die pad parts) 21 and a plurality of leads 22 which are arranged around the semiconductor element mounting parts 21. Next, as shown in FIG. 2A, in an adhesive sheet attaching step, the adhesive sheet 10 of the present invention is attached on one surface of the lead frame 20 such that the adhesive layer (not shown in the figures) of the adhesive sheet 10 is attached to the lead frame 20. Moreover, a laminate method is suitable for attaching the adhesive sheet 10 on the lead frame 20. Then, as shown in FIG. 2B, in a die attaching step, the semiconductor elements 30, such as IC chips, are mounted on the semiconductor element mounting parts 21 of the lead frame 20 using a die attaching agent (not shown in the figures) from the side at which the adhesive sheet 10 is not adhered.

In order to prevent the adhesion of the out gas components, which are generated from the adhesive sheet and the die attaching agent due to the heat applied thereto just before the wire bonding step, and decrease of yielding of the semiconductor devices due to wire connecting defects, the adhesive sheet, die attaching agent, and lead frame mounting IC chips may be subjected to plasma-cleaning.

As shown in FIG. 2C, in a wire bonding step, the semiconductor elements 30 and the leads 22 of the lead frame 20 are electrically connected with bonding wires 31, such as golden wires. Next, as shown in FIG. 2D, in a resin sealing step, the product which is prepared by the previous steps and is shown in FIG. 2C, is put into a die, and this is transfer-molded using a sealing resin (mold agent) 40, and the semiconductor elements 30 are sealed with the sealing resin 40.

After that, as shown in FIG. 2E, in an adhesive sheet peeling step, a QFN unit 60, in which a plurality of QFNs 50 are arranged, is prepared by peeling the adhesive sheet 10 from the sealing resin 40 and the lead frame 20. In a dicing step, which is the last step,

molding) under conditions in which the heating temperature was 180°C, the pressure was 10M Pa, and the operation time was 3 minutes. The obtained 64 packages after the resin sealing step were examined, and number of packages, in which the sealing resin attaches at external connection parts of the lead (the surface of the lead at which the adhesive sheet is attached), is denoted by a number of mold flashes.

3. Detection method for adhesive transfer

Using lead frames after evaluation of mold flash, adhesive transfer is detected.

First, the adhesive sheet was peeled from the lead frame with a peel speed of 500 mm/min.

After peeling the adhesive sheet, the 64 packages were examined, and the number of packages, in which the adhesive was transferred to the external connection parts of the lead, that is, the surface of the lead at which the adhesive sheet was attached, is denoted by the number of adhesive transfer.

4. Measurement method for Adhesive strength

The adhesive sheets obtained in the Examples and Comparative Examples were cut such that the widths thereof were 1 cm, and these were attached on a copper plate having dimensions of 50 mm x 100 mm x 0.25 mm thick (trade name: MF-202, marketed by MITSUBISHI METECS) and the copper plate plated with gold by a roll-lamination method. The plate was subjected to the same heat treatments as those in the die attaching step (at 175°C for 1 hour) and the mold resin step (at 180°C for 4 hours), and then cooled to room temperature. After that, the resulting laminate was heated to 150°C, and then the peel strength was measured when the adhesive layer of the obtained laminate was peeled from the plate such that the peeled adhesive layer forms an angle of 90° with respect to the plate. While changing the heated temperature from 150 to 200°C, this measurement was carried out at every 5°C in temperature rise. Moreover, the adhesive strength is the smallest peel strength in the heated temperature range from 150 to 200°C.

as shown in FIG. 2F, a plurality of QFNs 50 are prepared simultaneously by dicing the prepared QFN unit 60 along the outer surface of the QFNs 50.

Below, the adhesive sheet, the semiconductor device, and the production method for a semiconductor device of the present invention will be explained in detailed referring to Examples and Comparative Examples. However, the present invention is not limited to the following Examples.

The evaluation methods for evaluating the resulting adhesive layer and the adhesive sheet of Examples and Comparative Examples will be explained. The evaluations were carried out as follows.

Measurement method for Storage modulus

The release film with the adhesive layer was obtained by applying the adhesive coating obtained in the Examples and Comparative Examples on the release film and drying the adhesive coating under the same conditions as those in the producing process for the adhesive sheet, and this was further heated under the same conditions (at 175°C for 2 hours) as those in the die attaching step. Specifically, the adhesive coating was applying such that the thickness after drying was 0.1 mm, this was dried. The obtained sample was cut, and test pieces having a size of 5 mm x 30 mm were obtained. Using an elastic modulus measuring machine (marketed by Orientec Co., Ltd.; trade name: RHEOVIBRON DDV-II), the storage modulus of the adhesive layer was measured under conditions in which the frequency was 11 Hz, the rate of temperature increase was 3°C/min., and the measurement temperature range was 150 to 250°C. The results were shown in the following tables. The storage modulus in the following tables is the smallest storage modulus in the measurement temperature range from 150 to 250°C.

Evaluation of the adhesive sheet

1. Detection method for wire bonding defects

The obtained adhesive sheet in the Examples and Comparative Examples was attached on a lead frame for QFNs (total size: 200 mm x 60 mm; copper lead frame plated with Au-Pd-Ni; 4 x 16 (64) QFNs; package size; 10 mm x 10 mm; 84 pins) by a lamination method. Dummy chips (dimensions of 6 mm x 6 mm x 0.4 mm thick) evaporated with aluminum were mounted on the semiconductor element mounting parts of the lead frame, using an epoxy based die attaching agent.

After that, without plasma-cleaning, the dummy chips and leads were electrically connected with golden wires using a wire bonder (trade name: UTC-470BI, marketed by Shinkawa Co., Ltd.) under conditions in which the heat temperature was 210°C, the US Power: 30, the load was 0.59N, and the operation time was 10 msec/pin. The obtained 64 packages were examined, and the number of packages, in which a connection defect occurs in the leads, is denoted by the number of wire bonding defects.

In some Examples and Comparative Examples, after mounting dummy chips on the semiconductor element mounting parts of the lead frame, plasma-cleaning was conducted. The plasma-cleaning was conducted using a plasma etching device (trade name: V1000, marketed by Yamato Chemical Industry Co., Ltd.) under conditions in which the use gas was Ar, the gas flow rate: 45 sccm, the RF output power: 450W, and the operation time was 5 minutes.

2. Detection method for Mold flash

Using the lead frame after evaluation of wire bonding defect, the mold flash was detected. The dummy chips were sealed with a epoxy based mold agent (biphenylepoxy based mold agent; filler amount: 85% by mass) in a manner of a transfer-mold (metallic

5. Measurement method for an amount of out gas from the adhesive sheet

A mass decrease ratio in the adhesive sheet was measured using a thermogravimetric decrease measurement device (trade name: EZ Star 6000-series, TG/DTA 6300, marketed by Seiko Instruments Inc.) under conditions in which the rate of temperature increase was 10°C/min., and the measurement temperature range was from 30 to 300°C. Smaller mass decrease ratio means the adhesive sheet generates smaller amount of out gas.

(Examples 1 to 4 and Comparative Examples 1 to 5

10 The adhesive coating having the composition shown in the Table 1 was obtained and then the adhesive sheet was prepared. Then the resulting adhesive layer and adhesive sheet were evaluated.

Specifically, the adhesive coating was prepared by mixing components in accordance with the composition (parts by mass) shown in Table 1, and dissolving the mixture in toluene. Next, as the heat resistant substrate, a polyimide resin film (trade name: KAPTON® 100EN; marketed by Du Pont-Toray Co., Ltd.; thickness: 25 µm; glass transition temperature: 300°C or greater; thermal expansion coefficient: 16 ppm/°C) was used. On the polyimide resin film, the obtained adhesive coating was applied such that the thickness after drying was 6 µm, and this was dried at 120°C for 5 minutes, and thereby the adhesive sheet comprising the adhesive layer was obtained.

Then, the wire bonding defects, mold flash, adhesive transfer, adhesive strength, and out gas amount were evaluated. The results are shown in Tables 2 and 3 (the out gas amount).

Table 1-1

		Example			
		1	2	3	4
Thermosetting resin component (a)	Epoxy resin *1	30	25	25	
	Phenol resin *2	30	25	25	
	Fluoroethylene vinyl ether copolymer having a functional group *9				30
Thermoplastic resin component (b)	Non reactive elastomer:	40		40	
	Acrylonitrile-butadiene copolymer *3				
	Reactive elastomer:		50		70
Fluorine based additive (c)	Maleic anhydride containing styrene-ethylene-butylene copolymer *6				
	Fluorine containing acrylic graft polymer *4	1.5			0.5
	Fluorine containing block polymer *7		0.5		
	Fluorine containing aliphatic polymeric ester *8			1.5	
Hardening agent	2-ethyl-4-methylimidazole *5	0.5	0.5	0.5	
	*10				1

Table 1-2

		Comparative Example				
		1	2	3	4	5
Thermosetting resin component (a)	Epoxy resin *1	45	35		35	
	Phenol resin *2	25	35		35	
	Epoxy resin *12			40		
	Phenol resin *13			20		
Thermoplastic resin component (b)	Non reactive elastomer:	40		40		
	Acrylonitrile-butadiene copolymer *3					
	Reactive elastomer:					
	Maleic anhydride containing styrene-ethylene-butylene copolymer *6					
	Reactive elastomer:		30		30	
	Epoxidized styrene-butadiene-styrene copolymer *11					
Others	Silicone oil *14			1.5	2	
	Silicone rubber *15					100
	Silicone rubber *16					0.5
Hardening agent	2-ethyl-4-methylimidazole *5	0.5	0.5	0.5	0.5	

*1: marketed by DAINIPPON INK AND CHEMICALS, INCORPORATED; trade name:
HP-7200

*2: marketed by NIPPON KAYAKU CO., LTD.; trade name: TPM

*3: marketed by ZEON CORPORATION; trade name: NIPOL® 1001

5 *4: marketed by Soken Chemical & Engineering Co. Ltd., trade name: CHEMTREE ®
LF-700, (solid content: 7.5% by mass, solvent: toluene and methyl ethyl ketone)

*5: marketed by Tokyo Chemical Industry Co., Ltd.

*6: marketed by Asahi Kasei Chemicals Corporation, trade name: TUFTECH ® M-1911

(*7: marketed by NOF Corporation, trade name: MODIPER® F-200 (solid content: 30%
10 by mass, solvent: methyl ethyl ketone, and methyl isobutyl ketone),

*8: marketed by 3M, trade name of NOVEC® F-4430

*9: marketed by ASAHI GLASS COMPANY, trade name: LUMIFLON ® LF916

*10: marketed by Nippon Polyurethane Industry Co., Ltd., trade name: Coronate L

*11: marketed by DAICEL CHEMICAL INDUSTRIES, LTD., trade name:
15 EPOFRIEND® AT 501

*12: marketed by Japan Epoxy Resins Co.,Ltd., trade name: EPIKOTE® 1001

(*13: Showa Highpolymer Co., Ltd., trade name: CKM-2400

*14: Shin-Etsu Chemical Co., Ltd., trade name: KF-105

*15: Dow Corning Toray Co., Ltd., trade name: SD4580

20 *16: Dow Corning Toray Co., Ltd., trade name: SRX212

Table 2

		Number of Wire bonding defect	Number of mold flash	Number of adhesive transfer	Adhesive strength (N/cm)	
					Non-gold plating	Gold plating
Example	1	0	0	0	1.05	0.82
	2	0	0	0	0.86	0.74
	3	0	0	0	1.30	1.07
	4	0	0	0	0.68	0.62
Comparative Example	1	2	0	63	5.43	4.36
	2	1	0	59	6.01	5.71
	3	17	0	0	1.26	1.00
	4	13	4	0	0.99	0.80
	5	20	32	41	0.64	0.67

Table 3

		Amount of out gas at 100°C (% by mass)	Amount of out gas at 200°C (% by mass)	Amount of out gas at 300°C (% by mass)
Example	1	0.3	0.6	0.8
	2	0.2	0.2	0.4
	3	0.2	0.2	0.5
	4	0.2	0.2	0.3
Comparative Example	1	0.3	0.7	0.8
	2	0.3	0.8	0.9
	3	0.7	1.3	1.7
	4	0.7	1.3	1.7
	5	0.7	1.0	1.4

5 Examples 5, 6, and 8

The adhesive coating was prepared by mixing components in accordance with the composition (parts by mass) shown in Table 4, and dissolving the mixture in toluene.

Next, as the heat resistant substrate, a polyimide resin film (trade name: KAPTON®

100EN; marketed by Du Pont-Toray Co., Ltd.; thickness: 25 μm; glass transition

10 temperature: 300°C or greater; thermal expansion coefficient: 16 ppm/°C) was used. On the polyimide resin film, the obtained adhesive coating was applied such that the thickness after drying was 6 μm, and this was dried at 120°C for 5 minutes, and thereby the adhesive sheet comprising the adhesive layer was obtained.

Examples 7, 10, and 11

The adhesive sheet of the Example was prepared in a manner identical to that of Example 5, except that the mixture having the composition shown in the following Table 4 was dissolved in methyl ethyl ketone.

Example 9

The adhesive coating was prepared by mixing components with the same composition (parts by mass) as that of Example 5. Next, as the heat resistant substrate, a copper foil (3/4 ounce; marketed by MITSUI KINZOKU; trade name: 3EC-VLP; thickness: 25 μm ; thermal expansion coefficient: 16 ppm/ $^{\circ}\text{C}$) was used. On a rough surface of the copper foil, the obtained adhesive coating was coated such that the thickness after drying was 8 μm , and this was dried at 120 $^{\circ}\text{C}$ for 5 minutes, and thereby the adhesive sheet of this Example was obtained.

Comparative Examples 6 and 7

The adhesive sheet of the Comparative Example was prepared in a manner identical to that of Example 5, except that the mixture having the composition shown in the following Table 4 was dissolved in methyl ethyl ketone.

Then, the adhesive sheet of Examples 5 to 11 and Comparative Examples 6 and 7 was subjected to a plasma-cleaning. The storage modulus, wire bonding defect, mold flash, adhesive transfer, and adhesive strength were evaluated using two kinds of the adhesive sheet, that is, the adhesive sheet which was subjected to a plasma-cleaning, and the adhesive sheet which was not subjected to a plasma-cleaning. The results are shown in Table 5.

Table 4

		Example										Comparative Example	
		5	6	7	8	9	10	11	6	7			
Thermosetting resin component (a1)	Fluorine resin *17	5	20	10	15	5							
	Epoxy resin A *18	5					10		10				
	Epoxy resin B *19							5		10	5		
	Phenol resin A *20						5			5			
	Phenol resin B *21							5			5		
Thermoplastic resin component (b1)	NBR *22	95				95				85			
	Ethylene-methylacrylate-glycidilemethacrylate copolymeric resin *23		80								90		
	Acrylic acid ester-glycidileacrylate-acrylonitrile copolymeric resin *24			90									
	SBR*25				85								
	Fluorine rubber *26							85	90				
Hardening agent *27		1	1	1	1	1							
Hardening accelerator (a1)/(b1)	Hardening accelerator *28								1	1	1		
		0.05	0.25	0.11	0.17	0.05	0.17	0.11	0.17	0.17	0.11		

*17: marketed by ASAHI GLASS COMPANY, trade name: LUMIFLON ® LF200F

*18: marketed by DAINIPPON INK AND CHEMICALS, INCORPORATED; trade name: HP-7200

*19: marketed by Japan Epoxy Resins Co.,Ltd., trade name: EPIKOTE® 828

*20: Showa Highpolymer Co., Ltd., trade name: CKM-2400

*21: Nippon Petrochemicals Company Limited, trade name:DPP-6095H

*22: Acrylonitrile-butadiene copolymeric resin, marketed by JSR Corporation, trade name: PNR-1H, mass average molecular weight: 330,000

*23: marketed by Sumitomo Chemical Co. Ltd., trade name: Bondfast 7M, mass average molecular weight: 70,000

*24: marketed by Teikoku Chemical Industries Co., Ltd., trade name: SG P-3DR, mass average molecular weight: 1,000,000

*25: styrene-butadiene copolymer, marketed by Asahi Kasei Chemicals Corporation, trade name: TUFTECH ® M-1911, mass average molecular weight: 110,000

*26: marketed by Du Pont Kabushiki Kaisya; trade name: VITON ® VTR-7119, mass average molecular weight: 300,000

*27: marketed by Nippon Polyurethane Industry Co., Ltd., trade name: Coronate L

*28: marketed by Shikoku Corp.; 2-ethyl-4-methylimidazole (2E4MZ)

Table 5

	Storage modulus (MPa)	Number of Wire bonding defect		Number of Mold flash		Number of Adhesive transfer		Adhesive strength (N/cm)	
		Non-plasma	Plasma	Non-plasma	Plasma	Non-plasma	Plasma	Non-plasma	Plasma
Example	5	0	0	0	0	0	0	2.35	1.96
	6	0	0	0	0	0	0	1.47	1.57
	7	0	0	0	0	0	0	0.98	0.78
	8	0	0	0	0	0	0	2.65	2.06
	9	0	0	0	0	0	0	2.35	1.96
	10	0	0	0	0	0	0	0.49	0.39
	11	0	0	0	0	0	0	0.59	0.44
Comparative Example	6	22	0	7	0	0	25	5.88	5.10
	7	31	0	8	8	0	29	6.86	5.98

As shown in Table 5, in the adhesive sheet of Examples which was subjected to a plasma-cleaning, none of wire bonding defects, mold flash, and adhesive transfer were completely generated. In contrast, in the adhesive sheet of Comparative Examples, number of adhesive transfer was large.

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Examples 12 and 13 and Comparative Examples 8 and 9

The adhesive coating was prepared by mixing components in accordance with the composition (parts by mass) shown in the following Table 6, and the mixture was dissolved in toluene so that the solid content was 20% by mass in Example 12 and Comparative Examples 8 and 9. In Example 13, the mixture was dissolved in methyl ethyl ketone so that the solid content was 20% by mass.

Using the resulting adhesive coating, the adhesive sheet was prepared and evaluated in a manner identical to that of Examples 1 to 4. The results are shown in Table 7.

15 In "Detection of mold flash" and "Detection of adhesive transfer" in Table 7 were evaluated in the following manner, not the above-mentioned manner.

(Detection method for Mold flash

The adhesive sheet prepared in Examples 12 and 13, and Comparative Examples 8 and 9 was attached on a lead frame for QFNs (total size: 200 mm x 60 mm; copper lead frame plated with Au-Pd-Ni; 4 x 16 (64) QFNs; package size; 10 mm x 10 mm; 84 pins) by a lamination method. After subjecting a heat treatment (at 175°C for 1 hour) corresponding to the die attaching step in an oven, the lead frame and the adhesive sheet were subjected to a plasma-cleaning. The plasma-cleaning was conducted using a plasma etching device (trade name: V1000, marketed by Yamato Chemical Industry Co.,

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Ltd.) under conditions in which the use gas was Ar, the gas flow rate: 45 sccm, the RF output power: 450W, and the operation time was 5 minutes. Then, the lead frame and the adhesive sheet were subjected to the same heat treatment (at 220°C for 15 minutes) as that in the wire bonding step on a hot plate. After that, the lead frame and the adhesive sheet were sealed with a epoxy based mold agent (biphenylepoxy based mold agent; filler amount: 85% by mass) in a manner of a transfer-mold (metallic molding) under conditions in which the heating temperature was 180°C, the pressure was 10M Pa, and the operation time was 3 minutes. The obtained 64 packages after the resin sealing step were examined, and number of packages, in which the sealing resin attaches at external connection parts of the lead (the surface of the lead at which the adhesive sheet was attached), was denoted by a number of mold flashes.

Detection method for adhesive transfer

Using lead frames after the evaluation of mold flash, adhesive transfer was detected. First, the adhesive sheet was peeled from the lead frame with a peel speed of 500 mm/min. Then, after peeling the adhesive sheet, the 64 packages were examined, and the number of packages, in which the adhesive was transferred to the surface, at which the adhesive sheet was peeled, containing a surface of the mold resin, was denoted by the number of adhesive transfer.

Table 6

		Example		Comparative Example	
		12	13	8	9
Fluorine resin	Fluoroethylene-vinyl ether copolymer containing a functional group *29	30	10		
	Fluoroethylene-vinyl ether copolymer containing a functional group *30			20	
Reactive elastomer	Maleic anhydride containing styrene-ethylene-butylene copolymer *31	70			
	Carboxyl group containing acrylonitrile-butadiene copolymer *32		90		
	Carboxyl group containing acrylonitrile-butadiene copolymer *33				20
Others	Non-reactive elastomer:			80	
	Styrene-butadiene copolymer *34				
	Non-fluorine resin: Phenol resin *35				40
	Non-fluorine resin: Epoxy resin *36				40
Hardening agent	*37	1	1	1	
	*38				8

*29: marketed by ASAHI GLASS COMPANY, trade name: LUMIFLON ® LF916

*30: marketed by ASAHI GLASS COMPANY, trade name: LUMIFLON ® LF200

*31: marketed by Asahi Kasei Chemicals Corporation, trade name: TUFTECH ® M-1911

(maleic anhydride containing styrene-ethylene-butylene copolymer, maleic anhydride:

5 styrene: ethylene-butylene (mass ratio) = 0.5:30:70)

*32: marketed by JSR Corporation, trade name: PNR-1H

*33: marketed by ZEON CORPORATION; trade name: NIPOL® 1072J

*34: marketed by Asahi Kasei Chemicals Corporation, trade name: TUFTECH ® H-1041

(*35: Nippon Petrochemicals Company Limited, trade name: DPP-6095H

10 *36: marketed by DAINIPPON INK AND CHEMICALS, INCORPORATED; trade name: HP-7200

*37: Nippon Polyurethane Industry Co., Ltd., trade name: Coronate L

*38: marketed by Tokyo Chemical Industry Co., Ltd. (2-ethyl-4-methylimidazole)

15 Table 7

	Number of Mold flash	Number of adhesive transfer
Example 12	0	0
Example 13	0	0
Comparative Example 8	15	64
Comparative Example 9	0	Peeling impossible

CLAIMS

1. An adhesive sheet for producing a semiconductor device which is detachably attached to a lead frame or a wiring substrate,
wherein the adhesive sheet comprises a substrate and an adhesive layer,
the adhesive layer comprises a thermosetting resin component (a), a thermoplastic resin component (b), and a fluorine based additive (c), and
the fluorine based additive (c) is at least one selected from the group consisting of fluorine containing graft polymers, fluorine containing block copolymers, and fluorine containing aliphatic polymer esters.
2. An adhesive sheet for producing a semiconductor device which is detachably attached to a lead frame or a wiring substrate,
wherein the adhesive sheet comprises a substrate and an adhesive layer,
the adhesive layer comprises fluorine resin, and
the adhesive layer comprise a thermosetting resin component (a1) and a thermoplastic resin component (b1) and at least one of the thermosetting resin component (a1) and the thermoplastic resin component (b1) is a fluorine containing olefin resin.
3. An adhesive sheet for producing a semiconductor device according to claim 2, wherein a mass ratio ((a1)/(b1)) between the thermosetting resin component (a1) and the thermoplastic resin component (b1) is in a range from 0.05 to 0.43.
4. An adhesive sheet for producing a semiconductor device according to claim 2, wherein a mass average molecular weight of the thermoplastic resin component (b1) is in a range from 2,000 to 1,000,000.
5. An adhesive sheet for producing a semiconductor device according to claim 2, wherein storage modulus of the adhesive layer after hardening is 0.1 MPa or greater in a temperature range from 150 to 250°C.

6. An adhesive sheet for producing a semiconductor device according to claim 1 or 2, wherein adhesive strength of the adhesive layer after hardening is in a range from 0.03 to 5 N/cm in a temperature range from 150 to 250°C.
7. An adhesive sheet for producing a semiconductor device according to claim 1 or 2, wherein the substrate is a heat resistant film having a glass transition temperature of 150°C or greater and a thermal expansion coefficient in a range from 5 to 50 ppm/°C.
8. An adhesive sheet for producing a semiconductor device according to claim 1 or 2, wherein the substrate is a metal foil having a thermal expansion coefficient in a range from 5 to 50 ppm/°C.
9. An adhesive sheet for producing a semiconductor device which is detachably attached to a lead frame or a wiring substrate,
wherein the adhesive sheet comprises a substrate and an adhesive layer, and
the adhesive layer comprises fluorine resin and a reactive elastomer.
10. An adhesive sheet for producing a semiconductor device according to claim 9, wherein the fluorine resin is one of copolymers obtained by polymerizing a monomer material containing fluoroolefins and vinyl ethers and copolymers obtained by polymerizing a monomer material containing fluoroolefins and vinyl esters.
11. An adhesive sheet for producing a semiconductor device according to claim 9, wherein the reactive elastomer is a maleic anhydride containing styrene-ethylene-butylene copolymer.
12. An adhesive sheet for producing a semiconductor device according to any one of claims 1, 2, and 9, wherein a protective film be provided on one surface of the adhesive layer.
13. A semiconductor device produced using the adhesive sheet according to any one

of claims 1, 2, and 9.

14. A production method for a semiconductor device comprising a step of manufacturing a semiconductor device using the adhesive sheet according to any one of claims 1, 2, and 9.