DESCRIPTION

TITLE OF THE INVENTION: RESIN SHEET FOR ELECTRONIC COMPONENT, RESIN SHEET FOR ELECTRONIC COMPONENT WITH PROTECTIVE FILM, AND SEMICONDUCTOR DEVICE AND METHOD FOR MANUFACTURING SAME

TECHNICAL FIELD

[0001]

The present invention relates to a resin sheet for an electronic component, a resin sheet for an electronic component with a protective film, and a semiconductor device, and a method for manufacturing the same.

BACKGROUND ART

[0002]

In recent years, electronic devices have been downsized and thinned, and accordingly, electronic and electric components to be mounted in the electronic devices have been required to be further downsized and thinned. Thus, in recent years, semiconductor electronic components have been downsized and thinned as a method such as surface mounting has been employed in place of conventional screwing and pin insertion. Electronic components such as MEMS (MICRO ELECTRO MECHANICAL SYSTEMS) have been no exception, and downsized and thinned by surface mounting particularly with a sheet-shaped resin (see, for example, Patent Documents 1 and 2).

[0003]

Among MEMS, electronic components such as pressure sensors, acceleration sensors, gyrosensors and SAW filters are absolutely required to have a hollow in the electronic component from a functional point of view.

[0004]

Fig. 1 shows a first semiconductor device according to the present invention, which is an example of an electronic component having a hollow structure. The structure itself has been used heretofore. Here, when a conventional resin material is used in a resin sheet 2 for an electronic component in Fig. 1, the hollow structure may be impaired with resin entering a hollow portion 4. Thus, hollow retainability at a higher level has been desired.

[0005]

The electronic component shown in Fig. 1 is covered with the resin sheet 2 for an electronic component up to the upper surface of a semiconductor chip 3 from a surface of a substrate 1. Thus, when the resin sheet 2 for an electronic component should be thin, external water vapor easily enters the hollow portion 4, leading to impairment of the sensitivity of the semiconductor chip 3. There is the problem that when heat is applied for the purpose of curing the thin resin sheet 2 for an electronic component or performing packaging, a gas remaining in the hollow portion 4 is expanded, leading to

deformation of the resin sheet 2 for an electronic component. Thus, a resin sheet for an electronic component which is thin but does not have the above-mentioned problems is desired.

[0006]

Fig. 2 shows a second semiconductor device according to the present invention, which is another example of an electronic component having a hollow structure. The structure itself has been used heretofore. In the case of the electronic component shown in Fig. 2, a hollow portion 9 has a large space volume, and therefore a gas remaining in the hollow portion 9 is more greatly expanded. In the case of the electronic component shown in Fig. 2, a resin sheet 7 for an electronic component exists only between a semiconductor chip mounting substrate 6 and a hollow structure forming substrate 10, and a distance between the hollow portion 9 and the outside is small, so that a movement distance for water vapor to enter the hollow portion 9 from the outside decreases. However, a conventional resin material does not have sufficiently low water vapor permeability, and when a conventional resin material is used in the resin sheet 7 for an electronic component as shown in Fig. 2, water vapor may permeate, leading to impairment of the sensitivity of a semiconductor chip 8. Thus, low-water vapor permeability at a higher level has been desired.

[0007]

Meanwhile, in recent years, improvement of resin

materials has been advanced. Regarding the hollow retainability, for example, a resin material having high viscosity/elasticity is used for one layer in a resin sheet for an electronic component which has a two-layer structure, and this resin material is disposed on a side adjacent to a hollow structure to prevent resin from entering the hollow structure. A resin sheet for an electronic component, the hollow retainability of which is improved in this way, has been developed (Patent Document 3). A resin material which is poor in hollow retainability but excellent in originally required properties of a resin sheet for an electronic component, such as film strength, is used for the other layer in the resin sheet for an electronic component to achieve the original purpose. Regarding the water vapor permeability, a technique has been developed in which the blending amount of an inorganic filler, and the like is controlled to reduce water vapor permeability (Patent Document 4).

[0008]

However, any of the above-mentioned techniques does not attain both hollow retainability and low-water vapor permeability, and further improvement is still desired.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0009]

Patent Document 1: Japanese Patent Laid-open Publication No. 2012-59743

Patent Document 2: Japanese Patent Laid-open Publication No. 2013-187242

Patent Document 3: Japanese Patent Laid-open Publication No. 2014-209612

Patent Document 4: Japanese Patent Laid-open Publication No. 2014-156516

SUMMARY

PROBLEMS TO BE SOLVED

[0010]

An object of the embodiments disclosed herein is to provide a resin sheet for an electronic component in which hollow retainability is improved by enhancing flexibility and film strength, and water vapor permeability is low.

SOLUTIONS TO THE PROBLEMS

[0011]

The present disclosure mainly has the following configuration for achieving the above-mentioned object. In an aspect, there is provided a resin sheet for an electronic component which includes: an acrylic copolymer (a); a thermosetting resin (b); and an inorganic filler (c); and a silane coupling agent (d) having an amino group, wherein the

acrylic copolymer (a) contains 30 mol% or more of an acrylonitrile unit in constituent monomer units, and the content of the acrylic copolymer (a) is 2 wt% to 5 wt% in the resin sheet for an electronic component.

[0011a]

In another aspect, there is provided a resin sheet for an electronic component with a protective film comprising the resin sheet for an electronic component as defined above, and a protective film.

[0011b]

In another aspect, there is provided a semiconductor device comprising: a semiconductor chip mounting substrate shaped to surround a semiconductor chip mounting surface; a semiconductor chip formed on the semiconductor chip mounting substrate; and a hollow structure forming substrate, the semiconductor chip mounting substrate being connected to the hollow structure forming substrate while the resin sheet for an electronic component as defined above is interposed between the semiconductor chip mounting substrate and the hollow structure forming substrate.

[0011c] In another aspect, there is provided a method for manufacturing a semiconductor device, the method comprising the steps of: (1) forming a semiconductor chip on a substrate; and (2) laminating the resin sheet for an electronic component as defined above from the semiconductor chip side so as to cover

the semiconductor chip formed on the substrate, in this order, the method including laminating the resin sheet for an electronic component so as to form a hollow structure between the substrate and the semiconductor chip.

[0011d]

In another aspect, there is provided a method for manufacturing a semiconductor device, the method comprising the steps of: (1') forming a semiconductor chip on a semiconductor chip mounting substrate shaped to surround a semiconductor chip mounting surface; (2') laminating the resin sheet for an electronic component as defined above on a connection surface of the semiconductor chip mounting substrate to a hollow structure forming substrate or a connection surface of the hollow structure forming substrate to the semiconductor chip mounting substrate; and (3') connecting the semiconductor chip mounting substrate to the hollow structure forming substrate while the resin sheet for an electronic component is interposed between the semiconductor chip mounting substrate and the hollow structure forming substrate.

EFFECTS

[0012]

According to the present invention, a resin sheet for an electronic component which attains both hollow retainability and low-water vapor permeability can be obtained. Accordingly,

even when the resin sheet for an electronic component has a hollow structure, the hollow structure is hardly impaired in the process of, for example, curing the resin sheet for an electronic component, so that a favorable semiconductor device can be obtained. Since water vapor permeability is low, the sensitivity of a semiconductor chip in the semiconductor device is hardly impaired.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

Fig. 1 shows a first semiconductor device according to the present invention.

Fig. 2 shows a second semiconductor device according to the present invention.

EMBODIMENT OF THE INVENTION

[0014]

A resin sheet for an electronic component according to the present invention includes: an acrylic copolymer (a); a thermosetting resin (b); and an inorganic filler (c); and a silane coupling agent (d) having an amino group, wherein the acrylic copolymer (a) contains 30 mol% or more of an acrylonitrile unit in constituent monomer units, and the content of the acrylic copolymer (a) is 2 wt% to 5 wt% in the resin sheet for an electronic component.

[0015]

The acrylic copolymer (a) in the present invention serves to make the resin sheet flexible, relax thermal stress, improve insulation quality due to low water absorbency, and the like. The acrylic copolymer (a) contains 30 mol% or more, preferably 35 mol% or more, of an acrylonitrile unit in constituent monomer units, so that the water vapor permeability of the resin sheet for an electronic component can be effectively reduced without impairing the flexibility of the resin sheet for an electronic component, and insulation quality can be improved. The acrylonitrile unit is a monomer unit having hydrophobicity. The amount of the acrylonitrile unit in the polymer increases, hydrophobicity as a polymer is enhanced, so that water vapor permeability can be reduced. By setting the amount of the acrylonitrile unit to 30 mol% or more, the water vapor

permeability of a 100 um-thick resin sheet under an environment at 40°C/90% RH can be kept at 50 g/(m^2•24h) or less while the flexibility of the resin sheet is retained.

[0016]

Here, the acrylonitrile unit is a constituent unit derived from acrylonitrile in raw material monomers in preparation of an acrylic copolymer by polymerizing the monomers. Constituent units other than the acrylonitrile unit are constituent units derived from monomers other than acrylonitrile in the raw material monomers.

[0017]

The kinds of constituent units other than the acrylonitrile in the acrylic copolymer (a) are not particularly limited. Examples of the acrylic acid ester or methacrylic acid ester include acrylic acid alkyl esters or methacrylic acid alkyl esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, pentyl acrylate, pentyl methacrylate, hexyl acrylate, hexyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, octyl acrylate and octyl methacrylate. Mention is also made of esters of acrylic acid with an alicyclic alcohol, such as cyclohexyl acrylate.

[0018]

The acrylic copolymer (a) may contain constituent units

other than the acrylic acid ester or methacrylic acid ester. Examples thereof include vinyl acetate, styrene, methylstyrene, chlorostyrene, vinylidene chloride and ethyl α-acetoxyacrylate.

[0019]

Preferably, the acrylic copolymer (a) has at least one functional group selected from an epoxy group, a hydroxyl group, an amino group, a hydroxyalkyl group, a vinyl group, a silanol group and an isocyanate group. Accordingly, binding with the later-described thermosetting resin (b) is strengthened, so that insulation quality is improved, resulting in improvement of the reliability of an electronic device. Particularly, the epoxy group is preferred from the viewpoint of compatibility with an epoxy resin.

[0020]

The content of the acrylic copolymer (a) in the present invention is 2 wt% to 5 wt%, preferably 2 to 3.5 wt% based on the total of the resin sheet for an electronic component. By setting the content of the acrylic copolymer (a) to 2 wt% or more, flexibility can be imparted to the resin composition to retain a shape as a sheet. By setting the content of the acrylic copolymer to 5 wt% or less, the water vapor permeability of the resin sheet for an electronic component can be effectively reduced, and insulation quality can be improved. This is because the water vapor permeability of the resin sheet for an

electronic component can be reduced by decreasing the content of the acrylic copolymer that is a constituent unit having the highest water vapor permeability in the constituent units of the resin sheet for an electronic component. By setting the amount of the acrylic copolymer to 5 wt% or less, the water vapor permeability of a 100 um-thick resin sheet at 40°C/90% RH can be kept at 50 g/(m^2•24h) or less.

[0021]

The thermosetting resin (b) in the present invention is not particularly limited, but it is preferably an epoxy resin.

[0022]

The epoxy resin that is preferably used in the present invention is preferably an epoxy resin having two or more epoxy groups in one molecule. Specific examples thereof include cresol-novolak-type epoxy resins, phenol-novolak-type epoxy resins, biphenyl-type epoxy resins, bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, naphthalene-type epoxy resins, dicyclopentadiene-type epoxy resins, linear aliphatic epoxy resins, alicyclic epoxy resins, heterocyclic epoxy resins and spiro ring-containing epoxy resins.

[0023]

Among these epoxy resins, epoxy resins having a low chlorine content and a low softening point, having flexibility and containing a large amount of difunctional components, such as biphenyl-type epoxy resins, bisphenol A-type epoxy resins,

bisphenol F-type epoxy resins, naphthalene-type epoxy resins and dicyclopentadiene-type epoxy resins, are preferably used in the present invention. Of course, these epoxy resins may be used in mixture.

[0024]

In the present invention, a curing agent may be used in combination with the thermosetting resin (b). The curing agent preferably used in the present invention is not particularly limited as long as it reacts with the epoxy resin to cure the epoxy resin. Specific examples thereof include phenol novolak resins, cresol novolak resins, various kinds of novolak resins synthesized from bisphenol A and resorcin, acid anhydrides such as maleic anhydride and pyromellitic anhydride, and aromatic amines such as diaminodiphenylsulphone. Among these curing agents, phenol novolak resins, cresol novolak resins, bisphenol A and diaminodiphenylsulphone are preferably used from the viewpoint of heat resistance and humidity resistance.

[0025]

In the present invention, a curing accelerator may be used in combination with the thermosetting resin (b). The curing accelerator preferably used in the present invention is not particularly limited as long as it accelerates a curing reaction. As specific examples thereof, imidazole compounds such as 2-methylimidazole, 2,4-dimethylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole,

2-phenyl-4-methylimidazole and 2-heptadecylimidazole; tertiary amine compounds such as triethylamine, benzyldimethylamine, α-methylbenzyldimethylamine, 2-(dimethylaminomethyl)phenol, 2,4,6-tris(dimethylaminomethyl)phenol and 1,8-diazabicyclo(5,4,0)undecene-7; and organic sulfone compounds such as triphenyl sulfone, triethyl sulfone, and tributyl sulfone are preferred. Particularly, imidazole compounds, triphenyl sulfone, 1,8-diazabicyclo(5,4,0)undecene-7 and so on are preferably used. These curing accelerators may be used in combination of two or more thereof according to a use, and the added amount thereof is preferably in the range of 0.1 to 30 parts by weight, more preferably in the range of 5 to 25 parts by weight based on 100 parts by weight of the thermosetting resin (b). Accordingly, storage stability is improved. By using the curing accelerator, the crosslinking density of the thermosetting resin is increased, flexibility is imparted to the resin sheet, water vapor permeability can be reduced, and insulation quality can be improved.

[0026]

Examples of the inorganic filler (c) in the present invention include fused silica, crystalline silica, calcium carbonate, magnesium carbonate, alumina, silicon nitride and titanium oxide, and fused silica is preferably used because of

its low moisture permeability. The fused silica mentioned here is amorphous silica having a true specific gravity of 2.3 or less. A method for manufacturing the fused silica is not necessarily required to involve a molten state, and any manufacturing method can be used. The fused silica can be manufactured by, for example, a method in which crystalline silica is melted, or a method in which fused silica is synthesized from various kinds of raw materials. The particle size of fused silica for use in the present invention is not particularly limited as long as the size does not affect an adhesive thickness and a distance between mounted components, and fused silica having a mean particle size of 20 μm or less is normally used. More preferably, two or more kinds of spherical fused silica having different mean particle sizes are used in combination for the purpose of improving fluidity during melting. Particularly preferably, spherical fused silica having a mean particle size of 3 μm or more and spherical fused silica having a mean particle size of 2 μm or less are used in combination. Still more preferably, spherical fused silica having a mean particle size of 3 μm or more and spherical fused silica having a mean particle size of 2 μm or less are mixed at a weight ratio of 95/5 to 30/70, and used.

[0027]

In the present invention, the content of the inorganic filler (c) is preferably 60 wt% to 90 wt% from the viewpoint

of water vapor permeability. The lower limit of the content of the inorganic filler (c) is more preferably 70 wt% or more, still more preferably 75 wt% or more. The upper limit of the content of the inorganic filler (c) is more preferably 88 wt% or less, still more preferably 83 wt% or less. By setting the content of the inorganic filler to 60 wt% or more, the water vapor permeability of the resin sheet for an electronic component can be further reduced, and by setting the content of the inorganic filler to 90 wt% or less, the resin sheet for an electronic component can be more easily processed into a sheet shape, and further, formed into a thin sheet having a thickness of 100 μm or less.

[0028]

The silane coupling agent (d) having an amino group in the present invention is excellent in compatibility with the acrylonitrile unit in the acrylic copolymer (a) because the silane coupling agent (d) has an amino group. Accordingly, the resin sheet for an electronic component according to the present invention has improved flexibility and film strength in a state before curing. Even when the resin sheet for an electronic component is heat-cured while being used for lamination or protection of electronic components having a hollow structure, deformation of the resin sheet for an electronic component, which is caused by thermal expansion of a remaining gas in the hollow portion, is small, so that lamination and protection can

be favorably performed under a wide range of processing conditions.

[0029]

Specific examples of the silane coupling agent (d) having an amino group include N-2(aminoethyl)-3-aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-phenyl-3-aminopropyltrimethoxysilane, 3-triethoxysilyl-N-(1,3-dimethyl-butylidene)propylamine and N-(vinylbenzyl)-2-aminoethyl-3-aminopropyltrimethoxysilane hydrochloride. Among them, N-phenyl-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane are preferred because they are more highly compatible with the acrylonitrile unit in the acrylic copolymer (a). The silane coupling agent having an amino group is excellent in compatibility between the acrylonitrile unit in the acrylic copolymer and the silane coupling agent, so that the flexibility of the resin sheet for an electronic component can be improved.

[0030]

In the present invention, the content of the silane coupling agent (d) having an amino group is preferably 0.4 to 3.0 in terms of a ratio of the minimum coverage area (m^2/g) of

the silane coupling agent used to the specific surface area of the inorganic filler (c). The lower limit of the content of the silane coupling agent (d) is more preferably 0.8 or more, and the upper limit of the content of the silane coupling agent (d) is more preferably 2.0 or less.

[0031]

The resin sheet for an electronic component according to the present invention may further contain various kinds of additives. Examples thereof may include flame retardants such as halogen compounds and phosphorus compounds; carbon black; various kinds of elastomers such as olefin-based copolymers, modified nitrile rubbers, modified butadiene rubbers and modified polybutadiene rubbers; filler surface treatment agents such as titanate-based coupling agents; and ion scavengers such as hydrotalcites.

[0032]

The resin sheet for an electronic component according to the present invention preferably has a water vapor permeability of 50 g/(m^2•24h) or less, more preferably 35 g/(m^2•24h) or less, still more preferably 20 g/(m^2•24h) or less at 40°C/90% RH when having a thickness of 100 μm. When water vapor permeability is low, insulation quality is improved, so that the reliability of an electronic device can be improved. Water vapor permeability can be measured in accordance with a method as described in JIS Z 0208 (1976) (cup method).

[0033]

When the thickness of the resin sheet for an electronic component is not 100 μm, water vapor permeability may be measured by the above-mentioned method, and converted in accordance with the following calculation formula.

[0034]

water vapor permeability at 40°C/90% RH with a thickness of 100 μm = measured value of water vapor permeability × (thickness (μm) of resin sheet for an electronic component which is used in measurement/100)

The resin sheet for an electronic component according to the present invention can be suitably used when a hollow structure is formed in an electronic component. The resin sheet for an electronic component according to the present invention is excellent in flexibility and film strength in a state before curing. When the resin sheet for an electronic component according to the present invention is used for lamination or protection of an electronic component having a hollow structure, a shape change is small even if a gas remaining in the hollow portion is expanded during heat curing.

[0035]

A method for manufacturing the resin sheet for an electronic component according to the present invention will now be described. As the method for manufacturing the resin sheet for an electronic component according to the present

invention, mention is made of a method in which melting/kneading is performed by a known kneading method using, for example, a Banbury mixer, a kneader roll, a single or twin screw extruder, a co-kneader and the like, and the resulting mixture is then molded into a sheet shape. The resin sheet for an electronic component can also be prepared in the following manner: a raw material is dissolved or dispersed in an organic solvent, for example one of or a mixture of two or more of aromatic solvents such as toluene, xylene and chlorobenzene, ketone-based solvents such as methyl ethyl ketone, methyl ketone and methyl isobutyl ketone, and aprotic polar solvents such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone, and the resulting solution or dispersion is then applied to a base material layer, for example a polyester film treated with silicone, fluorine, an alkyd compound or the like, and is dried. Particularly, the method in which a raw material is dissolved or dispersed, and the resulting solution or dispersion is then applied to a base material layer, and dried is preferred because a thinner film can be formed.

[0036]

A resin sheet for an electronic component with a protective film according to the present invention includes the resin sheet for an electronic component and a protective film. The protective film may be provided on only one surface, or both surfaces of the resin sheet for an electronic component. The

protective film mentioned in the present invention is not particularly limited as long as it is capable of protecting the surface of the resin sheet for an electronic component, and capable of being separated from the resin sheet for an electronic component. Examples of the protective film include polyester films and polyolefin films coated with silicone, a fluorine compound and an alkyd compound. The thickness of the protective film is not particularly limited, but it is generally 10 μm to 100 μm.

[0037]

A first semiconductor device according to the present invention includes: a substrate; a semiconductor chip formed on the substrate; and the resin sheet for an electronic component which is laminated so as to cover the semiconductor chip formed on the substrate, the first semiconductor device having a hollow structure formed between the substrate and the semiconductor chip.

[0038]

A second semiconductor device according to the present invention includes: a semiconductor chip mounting substrate shaped to surround a semiconductor chip mounting surface; a semiconductor chip formed on the semiconductor chip mounting substrate; and a hollow structure forming substrate, the semiconductor chip mounting substrate being connected to the hollow structure forming substrate while the resin sheet for

an electronic component is interposed therebetween.

[0039]

A method for manufacturing the first semiconductor device according to the present invention includes the steps of: (1) forming a semiconductor chip on a substrate; and (2) laminating a resin sheet for an electronic component from the semiconductor chip side so as to cover the semiconductor chip formed on the substrate, in this order, the method including laminating the resin sheet for an electronic component so as to form a hollow structure between the substrate and the semiconductor chip.

[0040]

A method for manufacturing the second semiconductor device according to the present invention includes the steps of: (1') forming a semiconductor chip on a semiconductor chip mounting substrate shaped to surround a semiconductor chip mounting surface; (2') laminating a resin sheet for an electronic component on a connection surface of the semiconductor chip mounting substrate to a hollow structure forming substrate or a connection surface of the hollow structure forming substrate to the semiconductor chip mounting substrate; and (3') connecting the semiconductor chip mounting substrate to the hollow structure forming substrate while the resin sheet for an electronic component is interposed therebetween, in this order.

[0041]

The semiconductor device is manufactured using the resin sheet for an electronic component, and thus permeation of water vapor into the hollow structure formed in the semiconductor device is suppressed, so that the sensitivity of the semiconductor chip is hardly impaired. Accordingly, a semiconductor device having high performance such as high sensitivity can be obtained. Even when the resin sheet for an electronic component is used for forming a hollow structure, resin is not deformed in lamination or heat-curing of the sheet, and a predetermined shape can be easily formed, so that excellent productivity is attained.

EXAMPLES

[0042]

Hereinafter, the present invention will be described in detail with reference to examples, but the present invention is not limited to these examples. Details of raw materials denoted by symbols in examples will be shown below.

[0043]

<Acrylic Copolymer 1>

106 g (2.00 mol) of acrylonitrile (manufactured by Wako Pure Chemical Industries, Ltd., special grade), 231 g (1.80 mol) of butyl acrylate (manufactured by Wako Pure Chemical Industries, Ltd., special grade), 28 g (0.20 mol) of glycidyl methacrylate (manufactured by Wako Pure Chemical Industries,

Ltd., special grade), and 2900 g of methyl ethyl ketone (manufactured by Wako Pure Chemical Industries, Ltd., first class grade) as a solvent were added in a reactor provided with a mixer and a cooler under a nitrogen atmosphere, the mixture was heated to 85°C under atmospheric pressure (1013 hPa), 0.001 g of 2-ethylhexyl mercaptoacetate (manufactured by Wako Pure Chemical Industries, Ltd.) as a chain transfer agent, and 0.002 g of azobisisobutyronitrile (manufactured by Wako Pure Chemical Industries, Ltd., V-60) as a polymerization initiator were further added, and the mixture was polymerized to a weight average molecular weight of 700,000. The weight average molecular weight was measured by a GPC (gel permeation chromatography) method (apparatus: GELPERMEATION CHROMATOGRAPH manufactured by TOSOH CORPORATION, column: TSK-GEL GMHXL (7.8 × 300 mm) manufactured by TOSOH CORPORATION), and calculated in terms of polystyrene.

[0044]

Thus, an acrylic copolymer 1 of acrylonitrile : butyl acrylate : glycidyl methacrylate at a molar ratio of 50 : 45 : 5 (weight average molecular weight: 700,000) is obtained.

[0045]

<Acrylic Copolymer 2>

106 g (2.00 mol) of acrylonitrile (manufactured by Wako Pure Chemical Industries, Ltd., special grade), 505 g (3.94 mol) of butyl acrylate (manufactured by Wako Pure Chemical

Industries, Ltd., special grade), 44 g (0.31 mol) of glycidyl methacrylate (manufactured by Wako Pure Chemical Industries, Ltd., special grade), and 6600 g of methyl ethyl ketone (manufactured by Wako Pure Chemical Industries, Ltd., first class grade) as a solvent were added in a reactor provided with a mixer and a cooler under a nitrogen atmosphere, the mixture was heated to 85°C under atmospheric pressure (1013 hPa), 0.001 g of 2-ethylhexyl mercaptoacetate (manufactured by Wako Pure Chemical Industries, Ltd.) as a chain transfer agent, and 0.002 g of azobisisobutyronitrile (manufactured by Wako Pure Chemical Industries, Ltd., V-60) as a polymerization initiator were further added, and the mixture was polymerized to a weight average molecular weight of 860,000. The weight average molecular weight was measured by the same method as that for the acrylic copolymer 1.

[0046]

Thus, an acrylic copolymer 2 of acrylonitrile : butyl acrylate : glycidyl methacrylate at a molar ratio of 32 : 63 : 5 (weight average molecular weight: 860,000) is obtained.

[0047]

<Acrylic Copolymer 3>

200 g (2.00 mol) of ethyl acrylate (manufactured by Wako Pure Chemical Industries, Ltd., special grade), 118 g (0.920 mol) of butyl acrylate (manufactured by Wako Pure Chemical Industries, Ltd., special grade), 22 g (0.155 mol) of glycidyl

methacrylate (manufactured by Wako Pure Chemical Industries, Ltd., special grade), and 3000 g of methyl ethyl ketone (manufactured by Wako Pure Chemical Industries, Ltd., first class grade) as a solvent were added in a reactor provided with a mixer and a cooler under a nitrogen atmosphere, the mixture was heated to 85°C under atmospheric pressure (1013 hPa), 0.001 g of 2-ethylhexyl mercaptoacetate (manufactured by Wako Pure Chemical Industries, Ltd.) as a chain transfer agent, and 0.001 g of azobisisobutyronitrile (manufactured by Wako Pure Chemical Industries, Ltd., V-60) as a polymerization initiator were further added, and the mixture was polymerized to a weight average molecular weight of 1,200,000. The weight average molecular weight was measured by the same method as that for the acrylic copolymer 1.

[0048]

Thus, an acrylic copolymer 3 of ethyl acrylate : butyl acrylate : glycidyl methacrylate at a molar ratio of 65 : 30 : 5 (weight average molecular weight: 1,200,000) is obtained.

[0049]

<Thermosetting Resin>

Bisphenol A-type epoxy resin (jER-828, epoxy equivalent: 190, manufactured by Mitsubishi Chemical Corporation, liquid at normal temperature, viscosity at 25°C: 14 Pa•s)

[0050]

<Curing Agent>

Novolak phenol (H-1, manufactured by Meiwa Plastic Industries, Ltd.)

[0051]

<Curing Accelerator>

2-heptadecylimidazole (C17Z, manufactured by SHIKOKU CHEMICALS CORPORATION)

[0052]

<Inorganic Filler>

Spherical fused silica (FB-5D, mean particle size: 5.0 μm, manufactured by Denka Company Limited)

Spherical fused silica (SO-C2, mean particle size: 0.5 μm, manufactured by Admatechs Company Limited)

[0053]

<Silane Coupling Agent>

N-phenyl-3-aminopropyltrimethoxysilane (KBM-573, manufactured by Shin-Etsu Chemical Co., Ltd.)

N-2-(aminoethyl)-3-aminopropylmethyldimethoxysilane (KBM-602, manufactured by Shin-Etsu Chemical Co., Ltd.)

Vinyltris(2-methoxyethoxy)silane (V0048, manufactured by Tokyo Chemical Industry Co., Ltd.).

[0054]

<Evaluation of Sheet-Shaped Film>

A laminate (50 μm-thick resin sheet for an electronic component) obtained in each of examples and comparative examples was wound around each of a core of 3 inches in diameter

and a core of 6 inches in diameter, and a sheet-shaped film was evaluated. The evaluation criteria are as described below. In the case where a resin sheet got a pinhole-like hole of 1 mm or more at the time of winding the resin sheet, the resin sheet was rated unable to be wound.

⊙: Able to be wound around both of the core of 3 inches in diameter and the core of 6 inches in diameter.

○: Unable to be wound around the core of 3 inches in diameter, and able to be wound around the core of 6 inches in diameter.

×: Unable to be wound around either of the core of 3 inches in diameter and the core of 6 inches in diameter.

[0055]

<Measurement of Water Vapor Permeability>

A 38 μm-thick polyethylene terephthalate film (PET 38 manufactured by LINTEC Corporation) with a silicone mold release agent and a protective film ("FILMBYNA" GT manufactured by FUJIMORI KOGYO CO., LTD) were removed from the laminate (100 μm-thick resin sheet for an electronic component) obtained in each of examples and comparative examples, and the resin sheet was heated and cured at 170°C for 2 hours. For the resulting cured product of the resin sheet for an electronic component, water vapor permeability was measured as specified in JIS Z 0208 (cup method). The measurement was made under the condition of 40°C/90% RH and 96 hours.

[0056]

<Hollow Sealing Test>

A laminate (50 μm-thick resin sheet for an electronic component) obtained in each of examples and comparative examples was cut to a square of 20 mm, and punched with a round hole of 5 mm at the center using a die. A 38 μm-thick polyethylene terephthalate film (PET 38 manufactured by LINTEC Corporation) with a silicone mold release agent and a protective film ("FILMBYNA" GT manufactured by FUJIMORI KOGYO CO., LTD) were separated from the punched laminate (50 μm-thick resin sheet for an electronic component) to obtain a punched resin sheet single film for an electronic component. The punched resin sheet single film for an electronic component was sandwiched between two sheets of cover glass (Micro Cover Glass No. 4 manufactured by Matsunami Glass Ind., Ltd.), pressing was performed at 60°C and 0.3 MPa for 1 minute, and the two sheets of cover glass and the punched resin sheet single film for an electronic component were laminated together to obtain a hollow sealing test specimen. The specimen was heated at 150°C for 2 hours, the length of a side of a hollow hole surrounded by the two sheets of cover glass and the resin sheet for an electronic component was measured, and a length larger than the initial value, 5 mm, was recorded.

[0057]

During heating at 150°C, a gas remaining in the hollow hole is expanded to spread the resin sheet for an electronic

component which surrounds the hollow portion. How much the resin sheet for an electronic component is deformed by expansion of the gas during heating can be determined by measuring an increase in diameter of the hollow hole after heating. The smaller the increase in diameter, the better the initial shape is retained, and hence the higher the hollow structure retaining performance.

[0058]

<Insulation Breakdown Test>

First, a 35 mm-square ceramic substrate was provided, and a two-layer flexible substrate (Metaloyal manufactured by Toray Advanced Film Co., Ltd., 25 μm-thick polyimide resin layer, 8 μm-thick copper foil) was applied at the center of the ceramic substrate to prepare an interdigitated array electrode of L/S = 15/15 μm.

[0059]

Subsequently, a laminate (50 μm-thick resin sheet for an electronic component) obtained in each of examples and comparative examples was cut to a square of 30 mm, and punched with a 20 mm-square hole at the center using a die. Next, a 38 μm-thick polyethylene terephthalate film (PET 38 manufactured by LINTEC Corporation) with a silicone mold release agent and a protective film ("FILMBYNA" GT manufactured by FUJIMORI KOGYO CO., LTD) were separated from the laminate (50 μm-thick resin sheet for an electronic component) to obtain

a punched resin sheet single film for an electronic component. The punched resin sheet single film for an electronic component was bonded onto the ceramic substrate so as to surround the circumference of the interdigitated array electrode on the ceramic substrate, and an additional 35 mm-square ceramic substrate was laminated thereon to prepare a structure of ceramic substrate/resin sheet for an electronic component·interdigitated array electrode/ceramic substrate.

[0060]

The structure was pressed at 60°C and 0.3 MPa for 1 minute to be bonded, and heated at 150°C for 2 hours in an oven to heat-cure the resin sheet for an electronic component, thereby obtaining an insulation breakdown test specimen. The specimen was placed under an environment at 40°C and 90% RH, a direct-current voltage of 12 V was applied to the interdigitated array electrode using a migration tester (MIG-8600B manufactured by IMV CORPORATION.), and an insulation resistance value after 336 hours was measured.

[0061]

Example 1

28.8 g of spherical fused silica (SO-C2, mean particle size: 0.5 μm, manufactured by Admatechs Company Limited) and 51.9 g of spherical fused silica (FB-5D, mean particle size: 5.0 μm, manufactured by Denka Company Limited) were added in a mixer, and 40 g of methyl isobutyl ketone was added.

Subsequently, 0.8 g of N-phenyl-3-aminopropyltrimethoxysilane (KBM-573, manufactured by Shin-Etsu Chemical Co., Ltd.) was sprayed by a sprayer, and mixed in the mixer. To the resulting mixture were added 2.5 g of an acrylic copolymer 1, 11.9 g of bisphenol A-type epoxy resin (jER-828, epoxy equivalent: 190, manufactured by Mitsubishi Chemical Corporation, liquid at normal temperature, viscosity at 25°C: 14 Pa•s), 4 g of novolak phenol (H-1, manufactured by Meiwa Plastic Industries, Ltd.) and 0.1 g of 2-heptadecylimidazole (C17Z, manufactured by SHIKOKU CHEMICALS CORPORATION), methyl isobutyl ketone was added so that the solid concentration was 70 wt%, and the mixture was stirred at 30°C, and treated by a homomixer to prepare an adhesive solution.

[0062]

The adhesive solution was applied to a 38 μm-thick polyethylene terephthalate film (PET 38 manufactured by LINTEC Corporation) with a silicone mold release agent by a bar coater so as to have a thickness of 50 μm after drying, and dried at 110°C for 5 minutes, and a protective film ("FILMBYNA" GT manufactured by FUJIMORI KOGYO CO., LTD) was laminated thereto to prepare a laminate (50 μm-thick resin sheet for an electronic component) in which a 38 μm-thick polyethylene terephthalate film (PET 38 manufactured by LINTEC Corporation) with a silicone mold release agent, a resin sheet for an electronic component and a protective film ("FILMBYNA" GT manufactured by FUJIMORI

KOGYO CO., LTD) were laminated in this order.

[0063]

Except that the adhesive solution was applied so as to have a thickness of 100 μm after drying, the same procedure as in preparation of the laminate (50 μm-thick resin sheet for an electronic component) was carried out to prepare a laminate (100 μm-thick resin sheet for an electronic component).

[0064]

Using the resulting laminate (50 μm-thick resin sheet for an electronic component), the sheet-shaped film was evaluated and the hollow sealing test and the insulation breakdown test were conducted as described above. Using the resulting laminate (100 μm-thick resin sheet for an electronic component), water vapor permeability was measured as described above. The results are shown in Table 1.

[0065]

Examples 2 to 11 and Comparative Examples 1 to 5

Except that the kind of each composition and the blending amount were changed as shown in Tables 1 and 2, the same procedure as in Example 1 was carried out to prepare a laminate (50 μm-thick resin sheet for an electronic component) and a laminate (100 μm-thick resin sheet for an electronic component) in which a 38 μm-thick polyethylene terephthalate film (PET 38 manufactured by LINTEC Corporation) with a silicone mold release agent, a resin sheet for an electronic component and

a protective film ("FILMBYNA" GT manufactured by FUJIMORI KOGYO CO., LTD) were laminated in this order.

[0066]

Using the resulting laminate (50 μm-thick resin sheet for an electronic component), the sheet-shaped film was evaluated and the hollow sealing test and the insulation breakdown test were conducted as described above. Using the resulting laminate (100 μm-thick resin sheet for an electronic component), water vapor permeability was measured as described above. The results are shown in Tables 1 and 2. For Comparative Example 1, it was impossible to measure water vapor permeability and conduct the hollow sealing test and the insulation breakdown test because the film applied by the bar coater had a pinhole-like hole of 1 mm or more.

[0067]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Acrylic copolymer (g)	Acrylic copolymer 1 [acrylonitrile : butyl acrylate : glycidyl methacrylate at a molar ratio of 50 : 45 : 5]	2.5	2.5	-	2.5	2.5	2.5	2.5	-	4	2.1	3
	Acrylic copolymer 2 [acrylonitrile : butyl acrylate : glycidyl methacrylate at a molar ratio of 32 : 63 : 5]	-	-	2.5	-	-	-	-	2.5	-	-	-
	Acrylic copolymer 3 [ethyl acrylate : butyl acrylate : glycidyl methacrylate at a molar ratio of 65 : 30 : 5]	-	-	-	-	-	-	-	-	-	-	-
Thermosetting resin (g)	Bisphenol A-type epoxy resin	11.9	11.9	11.9	17.3	23.3	8.2	6	11.9	10.8	0.9	35
Curing agent (g)	Novolak phenol	4	4	4	5.8	7.8	2.7	1.9	4	3.6	0.3	11.2
Curing accelerator (g)	2-heptadecylimidazole	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.3
Inorganic filler (g)	Spherical fused silica (SO-C2)	28.8	28.8	28.8	26.2	23.4	30.6	31.6	28.8	28.8	34.1	18.0
	Spherical fused silica (FB-5D)	51.9	51.9	51.9	47.3	42.1	55.1	57.0	51.9	51.9	61.6	32.0
Silane coupling agent (g) * The parenthesized value is a ratio of the minimum coverage area (m^2/g) of the silane coupling agent used to the specific surface area of the inorganic filler.	N-phenyl-3-aminopropyltrimethoxysilane	0.8 (1.0)	-	0.8 (1.0)	0.7 (1.0)	0.7 (1.0)	0.8 (1.0)	0.9 (1.0)	-	0.8 (1.0)	0.9 (1.0)	0.5 (1.0)
	N-2-(aminoethyl)-3-aminopropylmethyldimethoxysilane	-	0.8 (0.8)	-	-	-	-	-	0.8 (0.8)		-	-
	Vinyltris(2-methoxyethoxy)silane	-	-	-	-	-	-	-	-	-	-	-
Evaluation of sheet-shaped film		⊙	⊙	⊙	⊙	⊙	○	○	⊙	⊙	○	⊙
Water vapor permeability ($g/(m^2 \cdot 24h)$)		13	28	21	50	82	11	10	32	49	8	90
Hollow sealing test [μm]		38	120	80	52	72	30	22	140	47	18	89
Insulation breakdown test [Ω]		4×10^{13}	6×10^{11}	6×10^{12}	6×10^{10}	2×10^{10}	6×10^{13}	7×10^{13}	4×10^{11}	7×10^{10}	9×10^{13}	1×10^{10}

[0068]

[Table 2]

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Acrylic copolymer (g)	Acrylic copolymer 1 [acrylonitrile : butyl acrylate : glycidyl methacrylate at a molar ratio of 50 : 45 : 5]	1.5	10	-	2.5	2.5
	Acrylic copolymer 2 [acrylonitrile : butyl acrylate : glycidyl methacrylate at a molar ratio of 32 : 63 : 5]	-	-	-	-	-
	Acrylic copolymer 3 [ethyl acrylate : butyl acrylate : glycidyl methacrylate at a molar ratio of 65 : 30 : 5]	-	-	2.5	-	-
Thermosetting resin (g)	Bisphenol A-type epoxy resin	11.9	11.9	11.9	11.9	11.9
Curing agent (g)	Novolak phenol	4	4	4	4	4
Curing accelerator (g)	2-undecylimidazole	0.1	0.1	0.1	0.1	0.1
Inorganic filler (g)	Spherical fused silica (SO-C2)	28.8	28.8	28.8	28.8	28.8
	Spherical fused silica (FB-5D)	52.9	52.9	51.9	51.9	51.9
Silane coupling agent (g) * The parenthesized value is a ratio of the minimum coverage area (m^2/g) of the silane coupling agent used to the specific surface area of the inorganic filler.	N-phenyl-3-aminopropyltrimethoxysilane	0.8 (1.0)	0.8 (1.0)	0.8 (1.0)	-	-
	N-2-(aminoethyl)-3-aminopropylmethyldimethoxysilane	-	-	-	-	-
	Vinyltris(2-methoxyethoxy)silane	-	-	-	0.8 (1.1)	-
Evaluation of sheet-shaped film		×	⊙	⊙	⊙	○
Water vapor permeability ($g/(m^2 \cdot 24h)$)		-	125	45	47	24
Hollow sealing test [μm]		-	210	360	420	560
Insulation breakdown test [Ω]		-	4×10^9	6×10^{10}	6×10^{10}	2×10^{10}

DESCRIPTION OF REFERENCE SIGNS

[0069]

1: Substrate

2: Resin sheet for an electronic component

3: Semiconductor chip

4: Hollow portion

5: Solder ball

6: Semiconductor chip mounting substrate

7: Resin sheet for an electronic component

8: Semiconductor chip

9: Hollow portion

10: Hollow structure forming substrate

CLAIMS

1. A resin sheet for an electronic component comprising: an acrylic copolymer (a); a thermosetting resin (b); and an inorganic filler (c); and a silane coupling agent (d) having an amino group, wherein the acrylic copolymer (a) contains 30 mol% or more of an acrylonitrile unit in constituent monomer units, and the content of the acrylic copolymer (a) is 2 wt% to 5 wt% in the resin sheet for an electronic component.

2. The resin sheet for an electronic component according to claim 1, wherein the content of the inorganic filler (c) is 60 wt% to 90 wt% in the resin sheet for an electronic component.

3. The resin sheet for an electronic component according to claim 1 or 2, which has a water vapor permeability of 50 g/(m^2•24h) or less at 40°C/90% RH with a thickness of 100 μm.

4. The resin sheet for an electronic component according to any one of claims 1 to 3, which is used for forming a hollow structure.

5. A resin sheet for an electronic component with a protective film comprising the resin sheet for an electronic component according to any one of claims 1 to 4, and a protective

film.

6. A semiconductor device comprising: a substrate; a semiconductor chip formed on the substrate; and the resin sheet for an electronic component according to any one of claims 1 to 4, which is laminated so as to cover the semiconductor chip formed on the substrate, the semiconductor device having a hollow structure formed between the substrate and the semiconductor chip.

7. A semiconductor device comprising: a semiconductor chip mounting substrate shaped to surround a semiconductor chip mounting surface; a semiconductor chip formed on the semiconductor chip mounting substrate; and a hollow structure forming substrate, the semiconductor chip mounting substrate being connected to the hollow structure forming substrate while the resin sheet for an electronic component according to any one of claims 1 to 4 is interposed between the semiconductor chip mounting substrate and the hollow structure forming substrate.

8. A method for manufacturing a semiconductor device, the method comprising the steps of: (1) forming a semiconductor chip on a substrate; and (2) laminating the resin sheet for an electronic component according to any one of claims 1 to 4 from

the semiconductor chip side so as to cover the semiconductor chip formed on the substrate, in this order, the method including laminating the resin sheet for an electronic component so as to form a hollow structure between the substrate and the semiconductor chip.

9. A method for manufacturing a semiconductor device, the method comprising the steps of: (1') forming a semiconductor chip on a semiconductor chip mounting substrate shaped to surround a semiconductor chip mounting surface; (2') laminating the resin sheet for an electronic component according to any one of claims 1 to 4 on a connection surface of the semiconductor chip mounting substrate to a hollow structure forming substrate or a connection surface of the hollow structure forming substrate to the semiconductor chip mounting substrate; and (3') connecting the semiconductor chip mounting substrate to the hollow structure forming substrate while the resin sheet for an electronic component is interposed between the semiconductor chip mounting substrate and the hollow structure forming substrate.