

[DESCRIPTION]

[Title of Invention]

EPOXY RESIN COMPOSITION AND CURED PRODUCT OF SAME

[Technical Field]

[0001] The present invention relates to an epoxy resin composition, an epoxy resin cured product, and a semiconductor device, and, more specifically relates to an epoxy resin composition that makes it possible to obtain an epoxy resin cured product excellent in heat resistance and thermal decomposition stability and that is excellent in tracking resistance and moreover that is, in particular, suitable for power semiconductor sealing, and also to an epoxy resin cured product, and a semiconductor device.

[Background Art]

[0002] Epoxy resins are used in a wide range of industrial applications. One example of use thereof is the use as a sealing material for semiconductor devices, but the level of performance required from semiconductor devices has been rising in recent years, and the required power density has risen to a range that is difficult to reach with conventional Si devices. Under these circumstances, SiC power devices exemplify devices that are expected to have further enhanced power density and are being developed in recent years. However, in order to achieve higher power density, the temperature of a chip surface during operation reaches 200°C or higher. Therefore, it is desirable to develop a sealing

material that can withstand such temperature and maintain physical properties for 1,000 h or more.

[0003] In particular, in the field of vehicle-mounted semiconductor devices, the integration of various sensors and electronic control units, which are adapted to safety control, is advancing, and because such devices are exposed for a long time to heat generated by an engine and power modules or heat generated by the integration, there is an increasing demand for materials that can withstand high-temperature environments.

[0004] Furthermore, a demand has been growing not only for thermal durability but also for insulation performance due to increase in voltage and electric current. A circuit pitch width and a distance between lead terminals have become smaller not only in power semiconductor devices used at high voltage utilized in vehicles, trains, wind power generation, solar power generation, etc., but also in semiconductor packages that are becoming smaller and thinner, hence, a tracking resistance characteristic of 600 V or more is required for sealing materials and substrate materials in order to ensure a spatial distance and a creepage distance for electrically insulating such devices.

[0005] Effective methods for improving tracking resistance include 1) suppression of thermal/oxidative decomposition (increase in thermal decomposition start temperature, suppression of volatile gas content), 2) improvement of

electrical insulation at high temperatures (increase in glass transition temperature), and 3) suppression of carbonization (reduction of residual coal rate, blending of inorganic filler), and various methods have been proposed. For example, a semiconductor device sealed with a silicone resin as a sealing material having high tracking resistance on the surface and excellent workability (PTL 1), a flame-retardant non-halogen epoxy resin composition that is excellent in tracking resistance, includes halogens and antimony compounds at 0.1% by weight or less, and has a polycondensation product of a phenol, a compound having a triazine ring, or an aldehyde as at least one curing agent (PTL 2), and a sealing material for a semiconductor chip that includes an epoxidized cyclic conjugated diene polymer as a resin component and may include a conductive filler including an inorganic filling agent (PTL 3) have been proposed. Further, a resin composition for semiconductor sealing that includes an alicyclic epoxy resin system having a cyclohexane polyether skeleton, a dicyclopentadiene type phenol resin, and the like and does not include a benzene skeleton (PTL 4), and a resin composition for semiconductor sealing in which a metal hydroxide is mixed as an inorganic filler with an epoxy resin (PTL 5) have been proposed as resin compositions for semiconductor sealing that excel in tracking resistance, but such compositions have reduced heat resistance. Meanwhile, an epoxy resin composition for semiconductor sealing that includes an epoxy

resin, a curing agent, an inorganic filler and a spherical silicone powder has been disclosed (PTL 6), but this resin composition does not seek to improve tracking resistance. Further, a sealing resin composition including silicone rubber powder (PTL 7) is excellent in tracking property but is not sufficient in heat resistance. Furthermore, there is a concern that silicone rubber powder may cause contact failure when low-molecular components volatilize. An epoxy resin, an epoxy resin composition and a cured product having a biphenol-biphenylaralkyl structure as a structure having excellent heat resistance have already been disclosed (PTL 8 and PTL 9), but no tracking resistance is mentioned in relation thereto.

[Citation List]

[Patent Literature]

[0006] [PTL 1] Japanese Patent Application Publication No. H 3-151674

[PTL 2] Japanese Patent Application Publication No. H 11-209569

[PTL 3] Japanese Patent Application Publication No. 2003-20325

[PTL 4] Japanese Patent Application Publication No. 2005-213299

[PTL 5] Japanese Patent Application Publication No. 2008-143950

[PTL 6] Japanese Patent Application Publication No. 2009-275146

[PTL 7] Japanese Patent Application Publication No. 2013-203865

[PTL 8] WO 2011/074517

[PTL 9] Japanese Patent Application Publication No. 2013-209503

[Summary of Invention]

[0007] With the conventional techniques, it is difficult to achieve both a heat resistance of 200°C or higher and a tracking resistance of 600 V, because there is a trade-off relationship between tracking resistance, heat resistance and flame retardancy. Therefore, the present invention aims at providing an epoxy resin composition that is particularly suitable for power semiconductor sealing and makes it possible to obtain an epoxy resin cured product that is particularly excellent in tracking resistance and also excellent in balance thereof with heat resistance and in thermal decomposition stability, and also to provide a resin cured product and a semiconductor.

[0008] The present invention provides an epoxy resin composition including, as essential components, components (A) to (D) below:

(A) an aromatic epoxy resin represented by a general formula (1) below;

(B) a modifier selected from a non-aromatic epoxy resin and a non-silicone rubber having a 5% weight loss temperature of

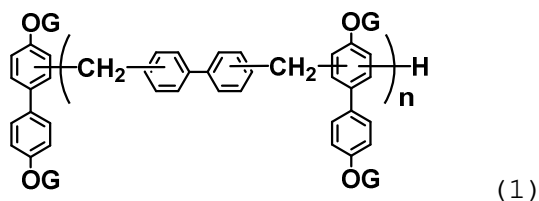
260°C or higher determined by TG/DTA measurement at a temperature rising rate of 10°C/min under a nitrogen stream;

(C) a curing agent; and

(D) a curing accelerator, wherein

the component (B) is contained in an amount of 1% by weight to 50% by weight with respect to a total amount of the components (A) to (D):

[C1]

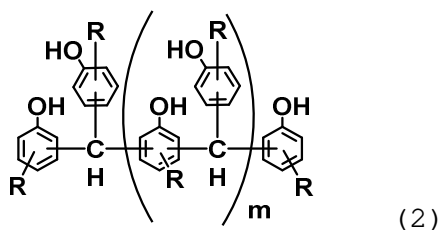


where, n represents a number of 0 to 20 and G represents a glycidyl group.

[0009] The component (B) can be exemplified by a modifier composed of a bifunctional epoxy resin including an epoxy resin of at least one kind selected from glycidyl esters of divalent aliphatic carboxylic acids having 15 to 64 carbon atoms or glycidyl ethers of dihydric aliphatic alcohols having 15 to 64 carbon atoms, or a rubber-based modifier composed of a styrene rubber or an acrylic rubber.

[0010] The component (C) can be exemplified by a curing agent including a phenol resin represented by a general formula (2) below:

[C2]



where, R represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms and m represents a number of 0 or 1.

[0011] The present invention also provides an epoxy resin cured product obtained by curing the epoxy resin composition. Furthermore, the present invention provides a semiconductor device in which a semiconductor element is sealed with the epoxy resin composition.

[0012] According to the present invention, it is possible to provide an epoxy resin composition, an epoxy resin cured product, and a semiconductor device that achieve both tracking resistance and heat resistance, which are difficult to obtain with the conventional techniques. Further, the epoxy resin composition has excellent flowability and moldability, and the cured product thereof has excellent glass transition temperature of 200°C or higher, long-term thermal stability, and flame retardancy. Furthermore, since the cured product is of a non-silicone type, it is suitable for in-vehicle use.

[Description of Embodiments]

[0013] The present invention will be described in detail hereinbelow.

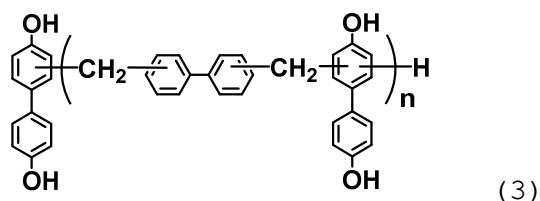
[0014] The epoxy resin composition of the present invention includes the following components (A) to (D) as essential components. (A) an aromatic epoxy resin represented by the general formula (1), (B) a modifier selected from a non-aromatic epoxy resin and a non-silicone rubber, (C) a curing agent, and (D) a curing accelerator.

[0015] The component (A) is an epoxy resin represented by the general formula (1), and since the resin has a biphenyl structure, it is also called a biphenylaralkyl-type epoxy resin. In the formula, n represents a number of 0 to 20, and G represents a glycidyl group. n is the number of repetitions and represents a number of 0 or more, and the average value (number average) thereof is 1.3 to 20, preferably 1.5 to 15, more preferably 1.7 to 10, and even more preferably 2 to 6. Further, from the viewpoint of reactivity and flowability, the amount of an $n = 0$ component in which n is 0 is preferably 30% by area or less as measured by gel permeation chromatography (GPC) measurement. Where the amount is more than that, the crystallinity becomes strong and the handling becomes difficult. Further, in the use by dissolution in an organic solvent for laminated plate application or the like, from the viewpoint of solvent solubility, the amount may be less than 15% by area and is preferably 10% by area or less. From the viewpoint of improving heat resistance, the amount of components with $n = 5$ or more is 15% by area or more, and preferably 20% by area or more. The weight average molecular

weight (Mw) measured by GPC is preferably 1,000 to 8,000, more preferably 2,000 to 7,000, and even more preferably 2,000 to 5,000.

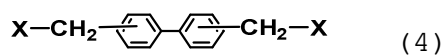
[0016] The epoxy resin can be produced by reacting a polyhydric hydroxy resin represented by a following general formula (3) with epichlorohydrin. Since this polyhydric hydroxy resin has a biphenyl structure, it is also called a biphenylaralkyl-type droxy resin. The biphenylaralkyl-type hydroxy resin can be obtained by reacting a biphenol with a biphenyl-based condensing agent represented by a following general formula (4).

[C3]



Here, n represents a number from 0 to 20.

[C4]



Here, X represents a hydroxyl group, a halogen atom or an alkoxy group having 1 to 6 carbon atoms.

[0017] Examples of biphenols as synthetic raw materials for a biphenylaralkyl-type hydroxy resin include 4,4'-dihydroxybiphenyls.

[0018] Specific examples of the biphenyl-based condensing agent include 4,4'-bishydroxymethylbiphenyl, 4,4'-

bischloromethylbiphenyl, 4,4'-bisbromomethylbiphenyl, 4,4'-bismethoxymethylbiphenyl, and 4,4'-bisethoxymethylbiphenyl. From the viewpoint of reactivity, 4,4'-bishydroxymethylbiphenyl and 4,4'-bischloromethylbiphenyl are preferable, and from the viewpoint of reducing ionic impurities, 4,4'-bishydroxymethylbiphenyl and 4,4'-bismethoxymethylbiphenyl are preferable.

[0019] The molar ratio for the reaction is preferably 1 mol or less, and generally within the range of 0.1 mol to 0.7 mol, and more preferably within the range of 0.2 mol to 0.5 mol of the biphenyl-based condensing agent with respect to 1 mol of 4,4'-dihydroxybiphenyl. Where the molar ratio is less than that, the crystallinity becomes strong, the solubility in epichlorohydrin at the time of synthesizing the epoxy resin is lowered, the melting point of the obtained epoxy resin becomes high, and the handleability is lowered. Meanwhile, where the molar ratio is larger than that, the crystallinity of the resin is lowered and the softening point and the melt viscosity are increased, so that handling workability and moldability are impaired.

[0020] Further, when using chloromethylbiphenyl as the condensing agent, the reaction can be performed without a catalyst, but normally this condensation reaction is carried out in the presence of an acidic catalyst. The acidic catalyst can be appropriately selected from well-known inorganic acids and organic acids, and examples thereof

include mineral acids such as hydrochloric acid, sulfuric acid, phosphoric acid, and the like, organic acids such as formic acid, oxalic acid, trifluoroacetic acid, p-toluenesulfonic acid, metasulfonic acid, trifluorometasulfonic acid, and the like, Lewis acids such as zinc chloride, aluminum chloride, iron chloride, boron trifluoride, and the like, solid acids, or the like.

[0021] This reaction is carried out at 10°C to 250°C for 1 h to 30 h. Further, during the reaction, an alcohol such as methanol, ethanol, propanol, butanol, ethylene glycol, methyl cellosolve, ethyl cellosolve, diethylene glycol dimethyl ether, triglyme, and the like, or an aromatic compound such as benzene, toluene, chlorobenzene, dichlorobenzene, and the like can be used as a solvent. After the completion of the reaction, the solvent, or water and alcohols produced by the condensation reaction are removed if necessary.

[0022] A method for producing the biphenylaralkyl-type epoxy resin represented by the general formula (1) by reacting the biphenylaralkyl-type hydroxy resin with epichlorohydrin will be described hereinbelow. This reaction can be performed in the same manner as the well-known epoxidation reaction.

[0023] For example, the method can include dissolving a biphenylaralkyl-type hydroxy resin in an excess of epichlorohydrin, and then conducting the reaction in the presence of an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide, or the like at 50°C to 150°C,

preferably 60°C to 120°C for 1 to 10 h. In this case, the amount of epichlorohydrin used is in the range of 0.8 mol to 2.0 mol, preferably 0.9 mol to 1.2 mol, based on 1 mol of the hydroxyl group in the polyhydric hydroxy resin. The target excess epichlorohydrin epoxy resin represented by the general formula (1) can be obtained by distilling off after completion of the reaction, dissolving the residue in a solvent such as toluene, methyl isobutyl ketone, and the like, washing with water to remove inorganic salts, and then distilling off the solvent. When carrying out the epoxidation reaction, a catalyst such as a quaternary ammonium salt or the like may be used.

[0024] As for the purity of the biphenylalkyl-type epoxy resin, in particular, the amount of hydrolyzable chlorine should be smaller from the viewpoint of improving the reliability of the electronic parts to which the resin is to be applied. Although not particularly limited, this amount is preferably 1,000 ppm or less, and more preferably 500 ppm or less. The hydrolyzable chlorine referred to in the present invention means a value measured by the following method. That is, this is the value obtained by dissolving 0.5 g of a sample in 30 ml of dioxane, adding 10 ml of 1N-KOH, boiling under reflux for 30 min, then cooling to room temperature, further adding 100 ml of 80% acetone water, and performing potentiometric titration with 0.002N-AgNO₃ aqueous solution.

[0025] The epoxy resin composition of the present invention may include an epoxy resin as another component in addition to the epoxy resin as the component (A). The epoxy resin as the other component is also referred to as a component (F).

The component (F) is preferably an aromatic epoxy resin obtained by epoxidizing a phenolic hydroxyl group.

As such epoxy resin, all the usual aromatic epoxy resins having two or more epoxy groups in a molecule can be used. Examples thereof include epoxy compounds of divalent phenols such as bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, 4,4'-biphenol, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl, resorcin, naphthalenediols, and the like; epoxy compounds of trivalent and higher phenols such as tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, o-cresol novolac, and the like; epoxy compounds of co-condensed resins obtained from dicyclopentadiene and phenols; epoxy compounds of co-condensed resins obtained from cresols, formaldehyde and alkoxy-substituted naphthalenes; epoxy compounds of phenol aralkyl resin obtained from phenols and para-xylylene dichloride or the like; epoxy compounds of biphenyl aralkyl type phenol resins obtained from phenols and bischloromethyl biphenyl or the like; epoxy compounds of naphthol aralkyl resins synthesized from naphthols and paraxylylene dichloride or the like; and the like. These epoxy resins can be used alone or

in combination of two or more. Further, in the epoxy resin composition of the present invention, the compounding amount of the epoxy resin represented by the general formula (1) is in the range of 5% by weight to 100% by weight, and preferably 60% by weight to 100% by weight in the whole epoxy resin.

[0026] The component (B) is a non-silicone type modifier selected from a non-aromatic epoxy resin or a non-silicone type rubber, and the modifier has a 5% weight loss temperature of 260°C or higher determined by TG/DTA measurement at a temperature rising rate of 10°C/min under a nitrogen stream. This modifier acts as a modifier for improving tracking resistance.

[0027] It is considered that when the modifier is blended, the modifier is phase-separated in the resin, so that the aggregation of the carbonized layer that occurs during thermal decomposition is suppressed, and improvement in tracking resistance can be expected.

[0028] By using a modifier with a 5% weight loss temperature of 260°C or higher, deterioration of mechanical strength can be prevented even when the epoxy resin composition is used at a high temperature of 200°C or higher.

[0029] The following advantages are obtained as a result of using a non-silicone type modifier as the modifier. Silicone-based modifiers such as silicone rubber may cause contact failure when low-molecular components volatilize, and may easily phase separate from the epoxy resin, making it

difficult to obtain a uniform composition, but the aforementioned modifier resolves these problems. The non-silicone type is also more advantageous in terms of cost.

[0030] The amount of the modifier is 1% by weight to 50% by weight, preferably 2% by weight to 30% by weight, based on the total of the above components (A) to (D).

From another point of view, the range may be from 1 part by weight to 50 parts by weight may with respect to 100 parts by weight of the total amount of resin components in the epoxy resin composition, but it is preferably 2 parts by weight to 30 parts by weight. Below this range, the effect of suppressing the aggregation of the carbonized layer is weak, whereas above this range, the glass transition temperature T_g of the cured product is lowered and the mechanical strength is also lowered.

[0031] The modifier is preferably dispersed in the form of particles or in a phase separation state of 10 μm or less. The particle diameter (median average diameter) is preferably 0.01 μm to 10 μm , more preferably 0.05 μm to 5 μm , and particularly preferably 0.1 μm to 1 μm .

[0032] These modifiers may be those well known in the art and are not particularly limited. As a modifier having excellent thermal stability, a bifunctional epoxy resin including, as an essential component, an epoxy resin of at least one kind selected from glycidyl esters of divalent aliphatic carboxylic acids having 15 to 64 carbon atoms or

glycidyl ethers of dihydric aliphatic alcohols having 15 to 64 carbon atoms is preferable.

Further, rubbers made of styrene rubber or acrylic rubber are excellent as modifiers as well.

[0033] Examples of the divalent aliphatic carboxylic acid having 15 to 64 carbon atoms include aliphatic dicarboxylic acids such as 2-dodecylsuccinic acid, hexadecanedioic acid, 8-hexadecenedioic acid, 8,9-diethylhexadecanedioic acid, eicosanedioic acid, 7-vinyl tetradecanedioic acid, 1,16-(6-ethylhexadecane)dicarboxylic acid, 1,18-(7,12-octadecadiene)dicarboxylic acid, 1,12-(diethyldodecane)dicarboxylic acid, and the like, and dimer acids having as a main component a dibasic acid having 36 carbon atoms which is obtained by an intermolecular reaction of two or more unsaturated fatty acids (linoleic acid, oleic acid, etc.), or hydrogenated dimer acids obtained by hydrogenating such dimer acids, but these examples are not particularly limiting. Epoxy resins of glycidyl esters of divalent aliphatic carboxylic acids having 15 to 64 carbon atoms can be obtained by converting these divalent aliphatic carboxylic acids into diglycidyl esters by a known epoxidation technique.

[0034] Examples of the dihydric aliphatic alcohol having 15 to 64 carbon atoms include long-chain aliphatic alcohols such as 1,15-pentadecanediol, 1,16-hexadecanediol, 1,18-octadecanediol, 1,19-nonadecanediol, and the like;

polyethylene glycols such as octaethylene glycol, nonaethylene glycol, and the like; polypropylene glycols such as pentapropylene glycol, hexapropylene glycol, and the like; cyclo ring-containing diols such as 4,4'-(propane-2,2-diyl)bis(cyclohexanol) and the like; dimer diols obtained by reducing a carboxyl group of the above-mentioned dimer acid or hydrogenated dimer acid to a hydroxyl group, hydrogenated dimer diols, and the like, but these examples are not particularly limiting. Epoxy resins of glycidyl ethers of dihydric aliphatic alcohols having 15 to 64 carbon atoms can be obtained by converting these dihydric aliphatic alcohols into diglycidyl ethers by a known epoxidation technique.

[0035] A rubber including a styrene (including substituted styrene) or an acryl (acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid, acrylonitrile, and the like) as a rubber component (monomer) or part of raw material of the rubber can be used as the styrene rubber and acrylic rubber. Further, non-silicone type natural rubber and diene type rubber such as butadiene rubber can also be used.

[0036] Examples of the styrene rubber include acrylonitrile butadiene styrene copolymer (ABS), acrylonitrile chlorinated polyethylene styrene copolymer (ACS), acrylonitrile ethylene propylene rubber styrene copolymer (AES), acrylonitrile styrene acrylate copolymer (ASA), methyl methacrylate acrylonitrile butadiene styrene copolymer (MABS), methyl methacrylate butadiene styrene copolymer (MBS), styrene

butadiene copolymer (SB), acrylonitrile styrene copolymer (SAN), styrene butadiene styrene block copolymer (SBS), styrene ethylene butylene styrene block copolymer (SEBS), styrene ethylene propylene styrene block copolymer (SEPS), styrene isoprene styrene block copolymer (SIS), acrylonitrile styrene dimethyl siloxane alkyl acrylate copolymer, and the like. Among them, from the viewpoint of reduction in elastic modulus and improving the impact resistance, a rubber obtained by copolymerization of styrene with a monomer having a saturated double bond, such as styrene butadiene copolymer (SB), methyl methacrylate butadiene styrene copolymer (MBS), acrylonitrile styrene dimethyl siloxane alkyl acrylate copolymer and the like, is preferable.

[0037] The acrylic rubber is preferably obtained, for example, by copolymerizing one or more kinds of alkyl (meth)acrylate and one or more kinds of vinyl monomer copolymerizable therewith. As the vinyl monomer copolymerizable with an alkyl (meth)acrylate, for example, a crosslinkable monomer is preferable, and examples thereof include aromatic polyfunctional vinyl monomers such as divinylbenzene, divinyltoluene, and the like; di- or tri(meth)acrylic acid esters of polyhydric alcohol such as ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, and the like; di- or triallyl compounds such as allyl (meth)acrylate, diallyl phthalate,

diallyl sebacate, triallyl triazine, triallyl cyanurate, triallyl isocyanurate, and the like. These may be used alone or in combination of two or more.

[0038] Component (C) is a curing agent for epoxy resins. As the curing agent, a known curing agent for epoxy resins can be used, but in the field where high electrical insulating properties are required, for example, in the field of semiconductor sealing materials, it is preferable to use polyhydric phenols as the curing agent. Specific examples of such curing agents are shown hereinbelow.

[0039] Examples of the polyhydric phenols include dihydric phenols such as bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, hydroquinone, resorcin, catechol, biphenols, naphthalenediols, and the like; trihydric and higher phenols such as tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, o-cresol novolac, naphthol novolac, dicyclopentadiene type phenol resin, phenol aralkyl resin, and the like; polyhydric phenolic compounds synthesized by a reaction of phenols, naphthols or dihydric phenols such as bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, catechol, naphthalenediols, and the like with a crosslinking agent such as formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, p-xylylene glycol, p-xylylene glycol dimethyl ether, divinylbenzene, diisopropenylbenzene, dimethoxymethylbiphenyls,

divinylbiphenyl, diisopropenylbiphenyls, and the like; biphenylaralkyl-type phenol resins obtained from phenols and bischloromethylbiphenyl or the like; naphtholaralkyl resins synthesized from naphthols and paraxylylene dichloride or the like; and the like.

[0040] Among these, the preferable phenol-based curing agent is the aralkyl type phenol resin represented by the general formula (2) hereinabove.

In the general formula (2), R is a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, preferably a hydrogen atom or an alkyl group having 1 to 3 carbon atoms. m represents a number of 0 or 1.

[0041] By using the aralkyl-type phenol resin or a curing agent including the same, a high Tg property of 200°C or higher required for a power device sealing material is revealed, and long-term thermal stability is manifested a glass state maintained during a long-term heat resistance test.

[0042] The aralkyl type phenol resin represented by the general formula (2) can be produced by reacting salicylaldehyde or p-hydroxyaldehyde with a phenolic hydroxyl group-containing compound.

[0043] The compounding amount of the curing agent is determined in consideration of the equivalence balance between the epoxy groups in the epoxy resin and the active hydrogen (hydroxyl groups in the case of polyhydric phenols) in the

curing agent. The equivalent ratio of the epoxy resin and the curing agent is usually in the range of 0.2 to 5.0, preferably 0.5 to 2.0, and more preferably 0.8 to 1.5. Where the equivalent ratio is larger or smaller than the above range, the curability of the epoxy resin composition is deteriorated, and the heat resistance and mechanical strength of the cured product are deteriorated.

[0044] In addition to the aromatic hydroxy compound, another type of curing agent may be blended as a curing agent component in the epoxy resin composition. Examples of the curing agent in this case include dicyandiamide, acid anhydrides, aromatic and aliphatic amines, and the like. In the epoxy resin composition of the present invention, these curing agents can be used singly or in a mixture of two or more thereof.

[0045] Examples of the acid anhydride curing agent include phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methylhymic anhydride, dodecynylsuccinic anhydride, nadic acid anhydride, trimellitic anhydride, and the like.

[0046] Examples of the amines include aromatic amines such as 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenylsulfone, m-phenylenediamine, p-xylylenediamine, and the like, and aliphatic amines such as

ethylenediamine, hexamethylenediamine, diethylenetriamine, triethylenetetramine, and the like.

[0047] Component (D) is a curing accelerator for the epoxy resin composition. The curing accelerator may be one well known in the technical field of epoxy resins and is not particularly limited. Examples thereof include amines, imidazoles, organic phosphines, Lewis acids, and the like.

Specific examples include tertiary amines such as 1,8-diazabicyclo(5,4,0)undecene-7, triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, tris(dimethylaminomethyl)phenol, and the like; imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 2-phenyl-4-methylimidazole, 2-heptadecylimidazole, and the like; organic phosphines such as tributylphosphine, methyldiphenylphosphine, triphenylphosphine, diphenylphosphine, phenylphosphine, and the like; tetrasubstituted phosphonium tetrasubstituted borates such as tetraphenylphosphonium tetraphenylborate, tetraphenylphosphonium ethyltriphenylborate, tetrabutylphosphonium tetrabutylborate, and the like; tetraphenylboron salts such as 2-ethyl-4-methylimidazole tetraphenylborate, N-methylmorpholine tetraphenylborate, and the like; and the like. The addition amount is usually in the range of 0.2 parts by weight to 5 parts by weight with respect to 100 parts by weight of the epoxy resin.

[0048] In the epoxy resin composition of the present invention, oligomers or polymer compounds such as polyesters, polyamides, polyimides, polyethers, polyurethanes, petroleum resins, indene resins, indene-coumarone resins, phenoxy resins, and the like may be blended, as appropriate, as other modifiers. The addition amount is usually in the range of 2 parts by weight to 30 parts by weight with respect to 100 parts by weight of the epoxy resin.

[0049] Further, an additive such as an inorganic filler, a pigment, a retardant, a thixotropic agent, a coupling agent, a fluidity improver, and the like can be blended in the epoxy resin composition of the present invention. Examples of the inorganic filler include silica powder such as spherical or crushed fused silica, crystalline silica, and the like, alumina powder, glass powder, or mica, talc, calcium carbonate, alumina, hydrated alumina, and the like. When the epoxy resin composition is used as a semiconductor sealing material, the blending amount of the filler preferably 70% by weight or more, and more preferably 80% by weight or more.

[0050] Examples of the pigment include organic or inorganic extender pigments, scale pigments, and the like. Examples of the thixotropic agent include castor oil type, aliphatic amide wax, oxidized polyethylene wax, organic bentonite type, and the like.

[0051] Further, if necessary, the resin composition of the present invention may include a release agent such as carnauba

wax, OP wax, and the like; a coupling agent such as γ -glycidoxypropyltrimethoxysilane and the like; a colorant such as carbon black and the like; a flame retardant such as antimony trioxide and the like; a lubricant such as calcium stearate and the like; and the like.

[0052] The epoxy resin composition of the present invention can be converted to a varnish state by partially or entirely dissolving in an organic solvent and then impregnated into a fibrous material such as a glass cloth, an aramid nonwoven fabric, a polyester nonwoven fabric, a liquid crystal polymer, or the like. A prepreg can be thereafter obtained by removing the solvent. When a solvent-insoluble matter such as an inorganic filler or the like is contained, it is not necessary to dissolve such matter, but it is desirable to put it in a suspended state to form as uniform solution as possible. Further, in some cases, a laminate can be obtained by applying on a sheet-shaped material such as a copper foil, a stainless steel foil, a polyimide film and a polyester film.

[0053] Where the epoxy resin composition of the present invention is heat-cured, an epoxy resin cured product can be obtained, and this cured product is excellent in terms of low hygroscopicity, high heat resistance, adhesiveness, flame retardancy, and the like. The cured product can be obtained by molding the epoxy resin composition by a method such as casting, compression molding or transfer molding. The temperature at this time is usually in the range of 120°C to

220°C. The epoxy resin composition of the present invention is particularly excellent as a sealing material. Further, the semiconductor device of the present invention can be obtained by sealing a semiconductor element with this epoxy resin composition.

Examples

[0054] The present invention will be specifically described with reference to synthesis examples, examples and comparative examples. However, the present invention is not limited to these. Unless specifically indicated otherwise, "part" represents part by weight and "%" represents % by weight. The measurement methods were as follows.

[0055] 1) Measurement of Epoxy Equivalent

The measurement was performed by using a potentiometric titrator, using chloroform as a solvent, adding a brominated tetraethylammonium acetic acid solution, and using a 0.1 mol/L perchloric acid-acid solution in the potentiometric titrator.

[0056] 2) Melting Point

A DSC peak temperature was determined by using a differential scanning calorimeter (EXSTAR6000 DSC/6200, manufactured by SII Nano Technology Inc.) under a condition of a temperature rising rate of 5°C/min. That is, this DSC peak temperature was taken as the melting point of the epoxy resin.

[0057] 3) Melt Viscosity

The measurement was performed at 150°C by using a CAP2000H type rotational viscometer manufactured by BROOKFIELD.

[0058] 4) Total Chlorine

The measurement was performed by dissolving 1.0 g of a sample in 25 ml of butyl carbitol, then adding 25 ml of 1N-KOH propylene glycol solution, refluxing for 10 min under heating, then cooling to room temperature, adding 100 ml of 80% acetone water, and performing potentiometric titration with a 0.002N- AgNO_3 aqueous solution.

[0059] 5) GPC Measurement

A configuration in which columns (TSKgel G4000HXL, TSKgel G3000HXL, TSKgel G2000HXL, manufactured by Tosoh Corporation) were connected in series to a main body (HLC-8220GPC, manufactured by Tosoh Corporation), and the column temperature was set to 40°C. Tetrahydrofuran (THF) was used as an eluent, the flow rate was set to 1 mL/min, and a differential refractive index detector was used. A total of 0.1 g of the sample was dissolved in 10 mL of THF, the solution was filtered with a microfilter, and 50 μL of the filtrate was used as a measurement sample. For data processing, GPC-8020 Model II version 6.00 manufactured by Tosoh Corporation was used.

[0060] 6) Glass Transition Temperature (T_g)

T_g was determined by using a thermomechanical measuring device (EXSTAR6000TMA/6100 manufactured by SII Nano Technology

Inc.) under a condition of a temperature rising rate of 10°C/min.

[0061] 7) 5% Weight Loss Temperature (Td5), Residual Coal Rate

A 5% weight loss temperature (Td5) was measured by using a thermogravimetric/differential thermal analyzer (EXSTAR6000TG/DTA6200, manufactured by SII Nano Technology Inc.) under a nitrogen atmosphere at a temperature rising rate of 10°C/min.

The weight loss at 700°C was also measured under the above conditions and converted to the resin component excluding the inorganic filler to calculate the residual coal rate of the resin component at 700°C.

[0062] 8) PTI Value (600 V)

According to IEC60112, a resin cured product (20×20×3 mm) was used as a test piece. Platinum electrodes with a tip angle of 30 degrees were used, and the electrodes were arranged at 4.0 mm and the facing angle was 60 degrees. The electrolytic solution used was a 0.1% ammonium chloride solution. After adjusting the state of the test piece at 23°C and 50% RH for 8 h, a voltage of 600 V was applied under the environment of 23°C and 50% RH, the electrolytic solution was dropped, and the number of drops before tracking fracture occurred on the test surface was determined. The test was conducted 5 times, and the number at which the tracking fracture did not occur at 600 V even after 50 drops was

measured. As the measuring device, HAT-112-3 manufactured by Yamayo-shikenki, Ltd. was used.

[0063] Synthesis Example 1

A 1,000 ml four-necked flask was charged with 75.0 g of 4,4'-dihydroxybiphenyl, 115.5 g of diethylene glycol dimethyl ether, and 40.5 g of 4,4'-bischloromethylbiphenyl, and the reaction was carried out for 20 h by raising the temperature to 170°C while stirring under a nitrogen stream. After the reaction, 46.4 g of diethylene glycol dimethyl ether was recovered. To this reaction mixture, 446.5 g of epichlorohydrin was added, and 69.4 g of 48% sodium hydroxide aqueous solution was added dropwise at 62°C over 4 h under reduced pressure (about 130 Torr). During this time, the produced water was removed from the system by azeotropic distillation with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After the dropping was completed, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, methyl isobutyl ketone was added, a salt was removed by washing with water, filtration and washing with water were carried out, and then methyl isobutyl ketone was distilled off under reduced pressure to obtain 141 g of an epoxy resin (epoxy resin 1). The epoxy equivalent of this epoxy resin was 198. Further, the peak temperature in the DSC measurement result of this epoxy resin was 126°C, and the melt viscosity at 150°C was 0.25 Pa·s.

[0064] Synthesis Example 2

A 1 L 4-necked flask was charged with 500 g of phenol (8.0 fold mol of dicyclopentadiene) and 9.5 g of boron trifluoride ether complex as an acid catalyst, and the temperature was raised to 120°C. Next, 88 g of dicyclopentadiene was added dropwise over 6 h for reaction while stirring at 120°C, and after aging at 130°C for 4 h, neutralization was performed and phenol was recovered. Subsequently, 179 g of a polyvalent hydroxy compound was obtained after dissolving in 300 g of MIBK, washing four times with water at 80°C, and distilling off MIBK under reduced pressure. The hydroxyl equivalent of the compound was 178 g/eq., the softening point was 93°C, and the weight average molecular weight was 422.

[0065] Synthesis Example 3

In a four-necked separable flask, 150 g of the resin obtained in Synthesis Example 2, 398 g of epichlorohydrin, and 59 g of diethylene glycol dimethyl ether were put and dissolved by stirring. After uniform dissolution, the reaction was conducted by keeping the temperature at 65°C under a reduced pressure of 130 mmHg, adding dropwise 68.2 g of a 48% sodium hydroxide aqueous solution over 4 h, separating epichlorohydrin and water distilled under reflux in a separation tank, returning the epichlorohydrin to the reaction vessel, and removing water outside the system. After the reaction was completed, the formed salt was removed by

filtration, the product was further washed with water and then epichlorohydrin was distilled off to obtain 157 g of an epoxy resin (epoxy resin 2). The epoxy equivalent of the obtained resin was 243 g/eq. The softening point was 84°C.

[0066] Synthesis Example 4

To a 2,000 ml four-necked flask, 300.0 g of dimer diol (Pripol 2033, manufactured by CRODA, hydroxyl equivalent 270 g/eq.), 308.3 g of epichlorohydrin, 120.0 g of toluene, and 6.2 g of water were charged, and dissolution was performed by raising the temperature to 50°C while stirring under a nitrogen stream. After the dissolution, 6.0 g of benzyltrimethylammonium chloride was added, and 13.6 g of 95.5% solid potassium hydroxide was divided and loaded over 2 h. After reacting for another 2.5 h, 300 g of toluene and 387.5 g of water were added, the salt produced by fractionation was removed, epichlorohydrin, toluene, and water were distilled off, and 543.2 g of toluene was added for dissolution at 80°C. Then, 12.3 g of a 48.8% potassium hydroxide aqueous solution was added to carry out a purification reaction, and after neutralization, washing with water and filtration, toluene was distilled off to obtain 325.9 g of a modifier (a) which was a liquid epoxy resin. The epoxy equivalent of the modifier (a) was 360 g/eq, and the viscosity at 25°C was 243 Pa·s. Further, Td5 was 324°C.

[0067] The abbreviations used in the examples are explained hereinbelow.

Epoxy Resin

Epoxy resin 1: epoxy resin obtained in Synthesis Example 1.

Epoxy resin 2: o-cresol novolac type epoxy resin (epoxy equivalent 200, softening point 65°C, manufactured by Nippon Steel & Sumikin Chemical Co., Ltd.).

Epoxy resin 3: epoxy resin obtained in Synthesis Example 3.

Modifier

Modifier a: modifier obtained in Synthesis Example 4.

Modifier b: radical control polymerization acrylic block copolymer having ABA structure with polybutyl acrylate as a soft component and polymethylene methacrylate as a hard component (NANOSTRENGTH M51, manufactured by ARKEMA, Td5: 291°C)

Modifier c: indene oligomer (IP-100; manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., softening point 101°C, 150°C, melt viscosity 1.3 Pa·s, Td5: 243°C).

Curing Agent

Curing agent 1: triphenol methane type polyhydric hydroxy resin (TPM-100, manufactured by Gunei Chemical Industry Co., Ltd., OH equivalent 97.5, softening point 105°C).

Curing agent 2: phenol novolac type polyhydric hydroxy resin (BRG-557, manufactured by Gunei Chemical Industry Co., Ltd., OH equivalent 105, softening point 80°C).

Curing Accelerator

2-Phenyl-4,5-dihydroxymethylimidazole (2PHZ-PW,
manufactured by Shikoku Chemicals Corp.)

Other

Silica filler: spherical silica (FB-8S, manufactured by
Denki Kagaku Kogyo Co., Ltd.)

Carnauba wax: (TOWAX171, manufactured by Toa Kasei Co.,
Ltd.)

Carbon black: (MA-100, manufactured by Mitsubishi
Chemical Corporation)

[0068] Example 1

As the epoxy resin components, 64.0 g of the epoxy resin
1 obtained in Synthesis Example 1, 5.1 g of the modifier (a),
and 32.9 g of the curing agent 1 were used. Further, 1.0 g of
a curing accelerator was used, and 498 g of a silica filler
was used as an inorganic filler. In addition, 0.5 g of
carnauba wax as a release agent and 0.5 g of carbon black as a
colorant were added and kneaded to obtain an epoxy resin
composition. A cured product test piece was obtained using
this epoxy resin composition under the conditions of a molding
temperature of 175°C for 3 min and a post cure temperature of
200°C for 5 h.

[0069] Examples 2 to 5, Comparative Examples 1 to 5

Epoxy resin compositions were prepared in the same manner
as in Example 1 by kneading an epoxy resin, a modifier, a
curing agent, an inorganic filler, a curing accelerator and
other additives in the blending ratios shown in Table 1.

Then, cured product test pieces were obtained using these epoxy resin compositions under the conditions of a molding temperature of 175°C for 3 min and a post cure temperature of 200°C for 5 h. The numerical values in the table indicate parts by weight in the composition.

[0070]

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Comp. Example 1	Comp. Example 2	Comp. Example 3	Comp. Example 4	Comp. Example 5
Epoxy resin 1	64.0	56.4	50.0	62.3	63.3	68.4		66.7		
Epoxy resin 2							66.9		63.5	
Epoxy resin 3										72.8
Modifier a	5.1	14.1	21.5	5.1						
Modifier b					5.1					
Modifier c									5.1	
Curing agent 1	32.9	31.5	30.5			33.6				29.2
Curing agent 2				34.6	33.6		35.1	35.3	33.4	
Silica filler	498.0	498.0	498.0	498.0	498.0	498.0	498.0	498.0	498.0	498.0
Curing accelerator	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Carbon black	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Carnauba wax	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tg (°C)	227	217	213	209	211	228	171	217	164	188
Td5 (°C)	395	390	382	394	390	395	379	395	372	411
Residual coal rate (% by weight)	40.7	36.8	33.4	42.5	43.4	43.1	36.2	48.1	35.6	16.9
PTI (600 V)	4/5	5/5	5/5	4/5	5/5	0/5	0/5	0/5	0/5	5/5

[0071] As is clear from these results, the epoxy resin compositions obtained in the examples were found to have both heat resistance having a glass transition temperature (T_g) of 200°C or higher and high tracking resistance.

[Industrial Applicability]

[0072] The present invention makes it possible to obtain an epoxy resin cured product having excellent tracking resistance, balance thereof with heat resistance, and also excellent thermal decomposition stability, the product being suitable as a semiconductor sealing material, in particular as a power semiconductor sealing material for vehicles.

[CLAIMS]

[Claim 1]

An epoxy resin composition including, as essential components, components (A) to (D) below:

(A) an aromatic epoxy resin represented by a general formula (1) below;

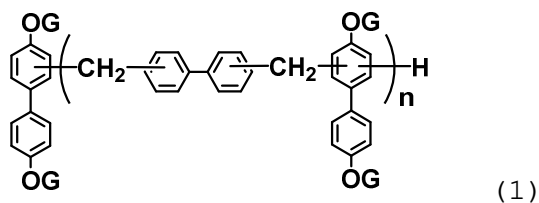
(B) a modifier selected from a non-aromatic epoxy resin and a non-silicone rubber having a 5% weight loss temperature of 260°C or higher, determined by TG/DTA measurement at a temperature rising rate of 10°C/min under a nitrogen stream;

(C) a curing agent; and

(D) a curing accelerator, wherein

the component (B) is contained in an amount of 1% by weight to 50% by weight with respect to a total amount of the components (A) to (D):

[C1]



where, n represents a number of 0 to 20 and G represents a glycidyl group.

[Claim 2]

The epoxy resin composition according to claim 1, wherein the component (B) is a modifier composed of a bifunctional epoxy resin including an epoxy resin of at least one kind

selected from glycidyl esters of divalent aliphatic carboxylic acids having 15 to 64 carbon atoms or glycidyl ethers of dihydric aliphatic alcohols having 15 to 64 carbon atoms.

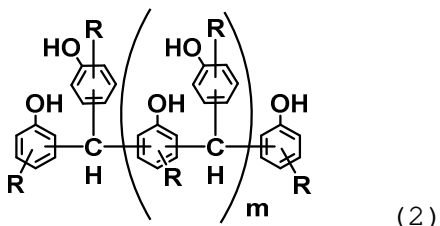
[Claim 3]

The epoxy resin composition according to claim 1, wherein the component (B) is a rubber-based modifier composed of a styrene rubber or an acrylic rubber

[Claim 4]

The epoxy resin composition according to claim 2 or 3, wherein the component (C) is a curing agent including a phenol resin represented by a general formula (2) below:

[C2]



where, R represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms and m represents a number of 0 or 1.

[Claim 5]

An epoxy resin cured product obtained by curing the epoxy resin composition according to any one of claims 1 to 4.

[Claim 6]

A semiconductor device, in which a semiconductor element is sealed with the epoxy resin composition according to any one of claims 1 to 4.