



(51) International Patent Classification:
H01L 33/56 (2010.01)

(21) International Application Number:
PCT/JP2014/073592

(22) International Filing Date:
29 August 2014 (29.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2013-184438 5 September 2013 (05.09.2013) JP

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.

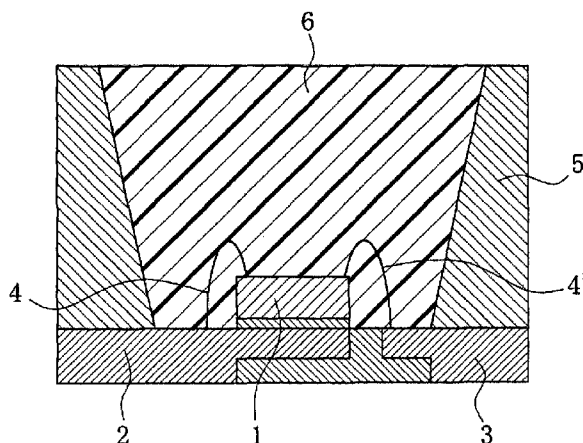
(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD OF MANUFACTURING OPTICAL SEMICONDUCTOR DEVICE AND OPTICAL SEMICONDUCTOR
DEVICE

FIG. 1



(57) Abstract: The present invention relates to a method of manufacturing an optical semiconductor device comprising a step of sealing an optical semiconductor element using a curable silicone composition, the curable silicone composition, although cured by a hydrosilylation reaction, being hydro silylation reaction catalyst free, or, if containing a hydrosilylation reaction catalyst, a content of the curable silicone composition being insufficient to cure the composition, and the optical semiconductor element being sealed in a state in which the curable silicone composition contacts a cured silicone that contains a hydrosilylation reaction catalyst. According to the present invention, a method of manufacturing an optical semiconductor device of which the sealing agent realizes storage stability, has good heat resistance, and can greatly resist discoloration can be provided; and an optical semiconductor device obtained by the manufacturing method can be provided.

DESCRIPTION**METHOD OF MANUFACTURING OPTICAL SEMICONDUCTOR DEVICE
AND OPTICAL SEMICONDUCTOR DEVICE****Technical Field**

5 [0001] The present invention relates to a method of manufacturing an optical semiconductor device, and particularly relates to a method of manufacturing an optical semiconductor device in which the storage stability of the sealing agent of the optical semiconductor device can be realized, and the sealing agent has good heat resistance and can greatly resist discoloration, and an optical semiconductor device obtained by the
10 manufacturing method.

[0002] Priority is claimed on Japanese Patent Application No. 2013-184438, filed on September 5, 2013, the content of which is incorporated herein by reference.

Background Art

15 [0003] Curable silicone compositions that cure due to a hydrosilylation reaction have been used as sealing agents, coating agents, lens-molding materials, light reflection materials, and the like for optical semiconductor elements in optical semiconductor devices such as photocouplers, light-emitting diodes, solid-state image sensors, and the like. For example, in Patent Document 1, a curable silicone composition is proposed, the composition being composed of an organopolysiloxane having an average of not less than
20 0.2 silicon-bonded alkenyl groups per molecule, an organopolysiloxane having a three-dimensional network structure, an organopolysiloxane having not less than two silicon-bonded hydrogen atoms per molecule, and a hydrosilylation reaction catalyst.

Additionally, in Patent Document 2, a curable silicone composition is proposed, the composition being composed of an organopolysiloxane having a silicon-bonded phenyl
25 group and a silicon-bonded alkenyl group, an organopolysiloxane having a silicon-bonded hydrogen atom, and a hydrosilylation reaction catalyst.

[0004] In such curable silicone compositions, a reaction control agent is added to suppress a hydrosilylation reaction because the hydrosilylation reaction proceeds even at room temperature; however, these compositions have the problem that viscosity increases
30 over time.

[0005] Furthermore, in such curable silicone compositions, a rise in viscosity is suppressed since the hydrosilylation reaction does not proceed unless a hydrosilylation

reaction catalyst is added. It is, however, considered to be necessary to add a hydrosilylation reaction catalyst because the reaction does not proceed to begin with, and it is also considered that a sealing agent or the like composed of a composition that does not contain the hydrosilylation reaction catalyst cannot be provided as a product.

- 5 [0006] Further, in addition to the above problems, the conventional cured silicones have the following problems. While high heat resistance is required of sealing agents of optical semiconductor elements, because the sealing agents directly receive heat generated from the elements, the conventional cured silicones yellow when exposed to high temperatures.

10 Prior Art Documents

Patent Documents

[0007]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 2006-213789

- 15 Patent Document 2: Japanese Unexamined Patent Application Publication No. 2009-185226

Summary of Invention

Technical Problem

- [0008] In consideration of the above, an object of the present invention is to provide a
20 method of manufacturing an optical semiconductor device in which the storage stability of the sealing agent of the optical semiconductor device can be realized, and the sealing agent has good heat resistance and can greatly resist discoloration even when exposed to high temperatures, and an optical semiconductor device obtained by the manufacturing method.

Solution to Problem

- 25 [0009] As a result of diligent research to solve the above problems, the present inventors discovered that discoloration arising due to the fact that the sealing agent contains a hydrosilylation reaction catalyst can be suppressed and good heat resistance can be realized by using a curable silicone composition that cures due to a hydrosilylation reaction and contains very little or no hydrosilylation reaction catalyst as the sealing agent
30 of an optical semiconductor element and by disposing cured silicone containing a hydrosilylation reaction catalyst as a member separate from the sealing agent. They also discovered that, because the curable silicone composition that forms the sealing agent does

not itself cure, a curable silicone composition, which is conventionally provided in a two-part form, can be provided in a one-part form, and therefore the complexity of the mixing operation of the two parts and the degassing operation after mixing can be avoided, and mistakes in compounding when mixing can be prevented.

5 [0010] That is to say, a first embodiment of the present invention is a method of manufacturing an optical semiconductor device comprising a step of sealing an optical semiconductor element using a curable silicone composition, wherein the curable silicone composition, although cured by a hydrosilylation reaction, does not contain a hydrosilylation reaction catalyst, or, if the curable silicone composition does contain the
10 hydrosilylation reaction catalyst, a content of the hydrosilylation reaction catalyst is not enough to cure the composition, and the optical semiconductor element is sealed in a state in which the curable silicone composition contacts cured silicone that contains the hydrosilylation reaction catalyst.

[0011] Furthermore, the curable silicone composition comprising: (A) at least one type
15 of organopolysiloxane having not less than two silicon-bonded alkenyl groups per molecule, and (B) at least one type of organopolysiloxane having not less than two silicon-bonded hydrogen atoms per molecule, and does not contain the hydrosilylation reaction catalyst, or, if curable silicone composition does contain the hydrosilylation reaction catalyst, the content of the hydrosilylation reaction catalyst is preferably not enough to cure
20 the composition.

[0012] The hydrosilylation reaction catalyst is preferably a platinum-based catalyst, and the curable silicone composition preferably does not contain a hydrosilylation reaction inhibitor.

[0013] Furthermore, the cured silicone is preferably a light reflection material,
25 substrate, a dam material, or a fluorescent substance-containing sheet.

[0014] Moreover, the cured silicone preferably contains at least one type of white pigment selected from the group consisting of titanium oxide, zinc oxide, barium titanate, barium sulfate, and zirconium oxide, and preferably contains at least one type of inorganic filler selected from the group consisting of non-spherical silica, spherical silica, and glass
30 fibers.

[0015] Another embodiment of the present invention is an optical semiconductor device manufactured by the above-described method of manufacturing an optical semiconductor device.

Effects of Invention

[0016] According to the present invention, a method of manufacturing an optical semiconductor device in which the sealing agent of the optical semiconductor device realizes storage stability, has good heat resistance, and can greatly resist discoloration can be provided; and an optical semiconductor device obtained by the manufacturing method can be provided.

[0017] Because the sealing agent is optically transparent or white even when it has been exposed to high temperature, the optical semiconductor device obtained by the method of manufacturing the present invention can also be used alone or in combination with various substrates for electrical and electronic parts or optical elements.

Brief Description of the Drawings

[0018]

FIG. 1 is a cross-sectional view of an LED that is an example of an optical semiconductor device of the present invention.

FIG. 2 is a cross-sectional view of an LED that is another example of the optical semiconductor device of the present invention.

FIG. 3 is a cross-sectional view of an LED that is yet another example of the optical semiconductor device of the present invention.

FIG. 4 is a cross-sectional view of an LED that is still another example of the optical semiconductor device of the present invention.

Detailed Description of the Invention

[0019] A method of manufacturing an optical semiconductor device and an optical semiconductor device according to the present invention will be specifically described below using the drawings.

[0020]

[Method of manufacturing optical semiconductor device]

The method of manufacturing an optical semiconductor device according to the present invention includes a step of sealing an optical semiconductor element using a curable silicone composition.

[0021] As a first embodiment of the present invention, as shown in FIG. 1, an optical semiconductor element 1 is sealed by disposing cured silicone (light reflection material 5 in FIG. 1) containing a hydrosilylation reaction catalyst, and then, using a curable silicone

composition that cures due to a hydrosilylation reaction and contains no hydrosilylation reaction catalyst, or, if the curable silicone composition does contain one, the content is not enough to cure the composition, putting a sealing agent 6 composed of that curable silicone composition in contact with the cured silicone 5.

5 [0022] Because the curable silicone composition contains extremely little or no hydrosilylation reaction catalyst, discoloration at high temperature caused by a hydrosilylation reaction catalyst can be suppressed. Furthermore, because the curable silicone composition curing reaction itself is effectively performed by a hydrosilylation reaction catalyst in the cured silicone that contacts the sealing agent, a sealing agent of
10 which the desired heat resistance and storage stability are assured can be formed.

[0023] As described above, there is a technical concept that, as a rule, the composition does not contain the hydrosilylation reaction catalyst from the viewpoint of suppressing discoloration at high temperature. Nevertheless, in cases where the composition unavoidably contains a hydrosilylation reaction catalyst and cases where the composition
15 contains a trace amount for some reason, it is stipulated that not only “the composition does not contain a hydrosilylation reaction catalyst,” but also “if the composition does contain one, the content is not enough to cure the composition.”

[0024]

[Cured silicone]

20 In the manufacturing method according to the present invention, cured silicone is disposed at a position so as to contact the sealing agent around the periphery of the semiconductor element.

[0025] The cured silicone means herein a material obtained by curing a prescribed curable silicone composition, and in the optical semiconductor device, the cured silicone is
25 not limited to a specific one provided that the cured silicone is a member disposed so as to contact the sealing agent. Specific examples include a light reflection material, a substrate, a dam material, and a fluorescent substance-containing sheet.

[0026] The composition that forms the cured silicone is not limited to a curable system, and may be any system provided that the system contains a hydrosilylation reaction
30 catalyst. It is, however, preferably a curable silicone composition comprising:

(a) an organopolysiloxane having not less than two silicon-bonded alkenyl groups per molecule,

(b) an organopolysiloxane having not less than two silicon-bonded hydrogen atoms per

molecule, and

(c) a hydrosilylation reaction catalyst.

[0027] Examples of the silicon-bonded alkenyl group in component (a) are a vinyl group, an aryl group, a butenyl group, a pentenyl group, and a hexenyl group, and a vinyl group is preferred. Examples of groups bonded to the silicon atom other than the alkenyl groups in component (a) include monovalent hydrocarbon groups such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, or a similar chain alkyl group; a cyclopentyl group, a cyclohexyl group, or a similar cycloalkyl group; a phenyl group, a tolyl group, a xylyl group, a naphthyl group, or a similar aryl group; a benzyl group, a phenethyl group, a 3-phenylpropyl group, or a similar aralkyl group; a chloromethyl group, a 3-chloropropyl group, a 3,3,3-trifluoropropyl group, a nonafluorobutylethyl group, or a similar halogenated hydrocarbon group. Examples of the molecular structure of component (a) include straight chain, cyclic, partially-branched straight chain, and branched, but at least one type of branched organopolysiloxane is preferably used as component (a) from the viewpoint that it can impart sufficient hardness and strength to the obtained cured silicone. The viscosity of component (a) is preferably from 1 to 10,000 mPa·s at 25°C.

[0028] Examples of the groups bonded to silicon other than a hydrogen atom in component (b) include the same monovalent hydrocarbon groups as described above.

Examples of the molecular structure of component (b) include straight chain, cyclic, partially-branched straight chain, and branched. Component (b) having a plurality of structures is preferably used in combination from the viewpoint of adjusting the hardness and strength of the obtained cured silicone. The viscosity of straight chain, cyclic, and partially-branched straight chain component (b) is preferably from 1 to 10,000 mPa·s at 25°C.

[0029] The compounded quantity of component (b) in the composition may be an amount sufficient to cure the curable silicone composition, and the amount of silicon-bonded hydrogen atoms in component (b) is preferably from 0.3 to 10 mol per 1 mol of the alkenyl groups in component (a). If the amount of silicon-bonded hydrogen atoms in component (b) per 1 mol of alkenyl groups in component (a) is below this range, it is undesirable because the composition tends to be insufficiently cured. On the other hand, if it exceeds this range, it is undesirable because the mechanical strength of the obtained cured silicone tends to be reduced.

[0030] The hydrosilylation reaction catalyst of component (c) is a catalyst for accelerating crosslinking of the composition, preferably a platinum-based catalyst. Examples of platinum-based catalysts include chloroplatinic acid, alcohol solutions of chloroplatinic acid, olefin complexes of platinum, alkenylsiloxane complexes of platinum, platinum black, and platinum-supported silica. The compounded quantity thereof is preferably from 1 to 1,000 ppm in mass units as platinum metal in the composition. It is preferably not less than 5 ppm from the viewpoint of accelerating curing of the curing silicone composition as the sealing agent, and not greater than 100 ppm from the viewpoint of increasing heat resistance of the obtained cured silicone.

[0031] Examples of other optional components that the composition may contain include hydrosilylation reaction inhibitors such as 3-methyl-1-butyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol, 3-phenyl-1-butyne-3-ol, or a similar alkyne alcohol; 3-methyl-3-penten-1-yne, and 3,5-dimethyl-3-hexen-1-yne, or a similar ene-yne compound; 1,3,5,7-tetramethyl-1,3,5-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane, and benzotriazole. The content of the hydrosilylation reaction inhibitor is preferably from 10 to 50,000 ppm of the composition in mass units.

[0032] When the cured silicone is used as a light reflection material for an optical semiconductor device, white pigment is preferably contained in the composition that constitutes the cured silicone for the purpose of increasing whiteness. Examples of the white pigment include metal oxides such as titanium oxide, alumina, zinc oxide, zirconium oxide and magnesium oxide; and barium sulfate, zinc sulfate, barium titanate, aluminum nitride, boron nitride, antimony oxide, and the like. Titanium oxide is preferred from the viewpoint of high light reflectance and blocking capability, and zinc oxide or barium titanate is preferred from the viewpoint of light reflectance in the UV range.

[0033] Although the shape and the average particle diameter of the white pigment are not limited, the average particle diameter is preferably from 0.05 to 10.0 μm , and particularly preferably from 0.1 to 5.0 μm . In order to increase the compatibility and dispersion ability of the white pigment with the resin and inorganic filler, the white pigment may be surface-treated using a silane coupling agent, silica, alumina, or the like.

[0034] The added quantity of white pigment is not less than 50 parts by mass, and preferably not less than 60 parts by mass, per 100 parts by mass of the total of components (a) and (b). This is because the light reflectance of the cured silicone is good when the content is not less than this lower limit.

[0035] When the cured silicone is used as light reflection material, because dimensional stability of the cured silicone is required, it is preferable if certain inorganic filler is contained in the composition that constitutes the cured silicone for the purpose of reducing the linear expansion coefficient of the obtained cured silicone. Examples of the inorganic filler include spherical silica, non-spherical silica, and glass fibers. Examples of the spherical silica of the inorganic filler include dry-method silica, wet-method silica, fused silica, and deflagration-method silica, but fused silica is preferred due to exhibiting good filling properties in the present composition. Examples of the non-spherical silica of the inorganic filler include quartz powder and glass beads, but quartz powder is preferred. Examples of the glass fibers of the inorganic filler include chopped glass fibers and milled glass fibers, but milled glass fibers are preferred.

[0036] The particle diameter of the spherical silica for the inorganic filler is not limited, but the average particle diameter is preferably from 0.1 to 50 μm , and particularly preferably from 0.5 to 30 μm . The particle diameter of the non-spherical silica for the inorganic filler is not limited, but the average particle diameter is preferably from 0.1 to 50 μm , and particularly preferably from 0.5 to 30 μm . The shape of the glass fibers for the inorganic filler is not limited, but the diameter of the fibers is preferably from 1 to 50 μm , and particularly preferably from 5 to 20 μm , and the length of the fibers is preferably from 5 to 500 μm , and particularly preferably from 10 to 300 μm .

[0037] The content of the inorganic filler is not less than 100 parts by mass, and preferably not less than 120 parts by mass, per 100 parts by mass of components (a) and (b). The linear expansion coefficient of the obtained cured product is low and dimensional stability is good when the content of inorganic filler is not less than the lower limit of this range.

[0038] The total content of the pigment component and the inorganic filler component is not great than 700 parts by mass, and preferably not greater than 600 parts by mass, per 100 parts by mass of components (a) and (b). When the total content of the pigment component and the inorganic filler component is not greater than the aforementioned upper limit, the viscosity of the obtained composition is good.

[0039] Additionally, when the cured silicone is used as a light reflection material, various additives may be compounded as necessary in the composition that constitutes the cured silicone. Other optional components that may be contained include inorganic fillers other than the spherical silica, non-spherical silica and glass fibers; fine powders of organic

resins such as polymethacrylate resins and silicone resins; mold release agents such as carnauba wax, higher fatty acids, metal salts of higher fatty acids, and methyl silicone oils; heat-resistant agents; flame retardants; solvents; and the like.

[0040] When the cured silicone is used as something other than a light reflection

5 material, for example, a fluorescent body-containing sheet, various additives may be compounded as necessary in the composition that constitutes the cured silicone. Other optional components that may be contained include inorganic fillers other than the spherical silica, non-spherical silica and glass fibers; fine powders of organic resins such as polymethacrylate resins and silicone resins; heat-resistant agents; dyes; pigments,
10 fluorescent substances; flame retardants; solvents; and the like.

[0041]

[Curable silicone composition]

With the method of manufacturing the present invention, a semiconductor element is sealed using a curable silicone composition that cures due to a hydrosilylation reaction
15 and does not contain a hydrosilylation reaction catalyst, or, if the curable silicone composition does contain one, the content is not enough to cure the composition.

[0042] Similar to the composition that constitutes the cured silicone, the curable silicone composition used in the present invention comprises:

(A) at least one type of organopolysiloxane having not less than two silicon-bonded
20 alkenyl groups per molecule, and

(B) at least one type of organopolysiloxane having not less than two silicon-bonded hydrogen atoms per molecule,

and does not contain a hydrosilylation reaction catalyst, or, if the curable silicone composition does contain one, the content is preferably not enough to cure the composition.

25 The aforementioned composition preferably does not contain a hydrosilylation reaction catalyst, or, if the curable silicone composition does contain one, the hydrosilylation reaction catalyst contains not more than 0.1 ppm metal atoms with respect to the mass of the composition.

[0043] Furthermore, the curable silicone composition that forms the cured silicone or

30 the sealing agent may contain various adhesion promoters to improve adhesion with various materials. Examples of such adhesion promoters include: organosilanes or linear, branched, or cyclic organosiloxane oligomers having approximately 4 to 20 silicon atoms having a trialkoxysiloxy group (e.g., a trimethoxysiloxy group or triethoxysiloxy group) or

a trialkoxysilylalkyl group (e.g., a trimethoxysilylethyl group or triethoxysilylethyl group), and a hydrosilyl group or alkenyl group (e.g., a vinyl group or allyl group); organosilanes or linear, branched, or cyclic organosiloxane oligomers having approximately 4 to 20 silicon atoms having a trialkoxysiloxy group or trialkoxysilylalkyl group, and a methacryloxyalkyl group (e.g., a 3-methacryloxypropyl group); organosilanes or linear, branched, or cyclic organosiloxane oligomers having approximately 4 to 20 silicon atoms having a trialkoxysiloxy group or trialkoxysilylalkyl group, and an epoxy group-bonded alkyl group (e.g., a 3-glycidoxypropyl group, 4-glycidoxybutyl group, 2-(3,4-epoxycyclohexyl)ethyl group, or 3-(3,4-epoxycyclohexyl)propyl group); and reaction products of aminoalkyl trialkoxysilanes and epoxy group-bonded alkyltrialkoxysilanes, and epoxy group-containing ethyl polysilicates. Specific examples of the adhesion promoters include: vinyl trimethoxysilane, allyl trimethoxysilane, allyl triethoxysilane, hydrogen triethoxysilane, 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl triethoxysilane, 2-(3,4-epoxy cyclohexyl)ethyl trimethoxysilane, 3-methacryloxypropyl trimethoxysilane, 3-methacryloxypropyl triethoxysilane, reaction products of 3-glycidoxypropyl triethoxysilane and 3-aminopropyl triethoxysilane, condensation reaction products of silanol group-terminated methylvinylsiloxane oligomers and 3-glycidoxypropyl trimethoxysilane, condensation reaction products of silanol group-terminated methylvinylsiloxane oligomers and 3-methacryloxypropyl triethoxysilane, tris(3-trimethoxysilylpropyl) isocyanurate, acid anhydrides, and the like. These adhesion promoters are preferably low-viscosity liquids, and their viscosity at 25°C is not particularly limited but is preferably from 1 to 500 mPa·s. The content of the adhesion promoter is not particularly limited, but is preferably from 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of components (A) and (B) in the composition. If the respective aforementioned adhesion promoters are added to the curable silicone composition, it does not matter if they are the same or different.

[0044] Furthermore, the curable silicone composition preferably does not contain a hydrosilylation reaction inhibitor. This is because there is no need to add a hydrosilylation reaction inhibitor because the curable silicone composition according to the present invention contains no or substantially no hydrosilylation reaction catalyst to begin with. The reason that curing of the curable silicone composition proceeds even without a hydrosilylation reaction catalyst is thought to be that the hydrosilylation reaction catalyst migrates during curing from the cured silicone that contacts it. However, when the

curable silicone composition contains a hydrosilylation reaction inhibitor, this migration is suppressed and curing ends up being slower.

[0045] When the curable silicone composition is used as a sealing agent or lens material for an optical semiconductor device, various fillers may be compounded as optional components in addition to the above-described mandatory components in order to improve mechanical strength of the silicone layer obtained by curing the composition, provided that the object of the present invention is preserved.

[0046] Examples of the fillers include inorganic reinforcing fillers such as precipitated silica, fumed silica, fused silica, and fumed titanium oxide; inorganic non-reinforcing fillers such as crushed quartz, diatomaceous earth, aluminosilicate, iron oxide, zinc oxide, and calcium carbonate; organic fillers such as polymethacrylate resin; and inorganic or organic fillers obtained by treating the surface with an organosilicon compound such as hexamethylsilazane, trimethylchlorosilane, polydimethylsiloxane, or polymethyl hydrogen siloxane.

[0047] The primary particle diameter of these fillers is preferably not greater than 0.5 μm , and more preferably not greater than 0.1 μm . The content thereof is controlled such that the light transmittance of the cured silicone of the curable silicone composition is not less than 80%, but it is typically not more than 10 percent by mass of the curable silicone composition, preferably not more than 5 percent by mass, and more preferably not more than 1 percent by mass. If transparency of the sealing agent and lens material is considered important, it is preferable not to compound any inorganic filler.

[0048] Additionally, if the curable silicone composition is used as a sealing agent or lens material of an optical semiconductor device, as components other than the aforementioned fillers, various additives may be compounded as necessary. Other optional components that may be contained include fine powders of organic resins such as polymethacrylate resins and silicone resins, heat-resistant agents, dyes, pigments, fluorescent substances, flame retardants, solvents, and the like.

[0049]

[Silicone composite material]

A composite material (silicone composite material) of the aforementioned cured silicone and a sealing agent or the like obtained using the aforementioned curable silicone composition will now be described.

[0050] The shape of the cured silicone that constitutes the silicone composite material

of the present invention is not particularly limited, but if a shape like that shown in FIG. 1 is used, the minimum distance from any point in the sealing agent 6 to the interface between the sealing agent 6 and the cured silicone 5 is preferably not greater than 5 mm, and more preferably not greater than 3 mm. According to the present invention, the curing catalyst required for heat curing of the curable silicone composition comes from the adjacently disposed cured silicone; therefore, when it is too far from the interface with the cured silicone, there is the possibility that the curing catalyst will not reach the curable silicone composition and curing will be insufficient. Due to this fact, a sealing agent composed of the curable silicone composition may be used in coating applications in which it is spread on the cured silicone, or in electronic materials applications in which the silicone compound itself is small, e.g., composite of light reflection material and sealing agent for optical semiconductor devices.

[0051] The curing temperature of the silicone composition that constitutes the cured silicone and the curing temperature of the aforementioned curable silicone composition are not particularly limited, but good curing is generally obtained from room temperature to 220°C. Curing at a temperature from 60°C to 180°C is preferable, and curing at a temperature from 80°C to 150°C is more preferable, because it results in strong adhesion between the silicone layer and substrate. Furthermore, step curing is preferable, wherein the composite is heated at from room temperature to 100°C, preferably from 60°C to 80°C, and is then heated at from 80°C to 180°C, preferably from 100°C to 150°C, because adhesion between the silicone layer and substrate is further improved in some cases.

[0052] In cases where the silicone composite material of the present invention is used in combination with another material such as a substrate, the material and shape of the substrate is not particularly limited. The substrate may be constructed from organic substances such as heat-curable resin and thermoplastic resin, or various structural bodies such as fabrics, non-woven fabrics or porous bodies, and the substrate may have various shapes such as a sheet, a rod, a hemisphere, a sphere and the like. Furthermore, various additional layers such as transparent acrylic resin layers may be provided as necessary on the surface of the silicone composite material of the present invention.

[0053] The silicone composite material of the present invention is not limited to being incorporated into an optical semiconductor device. The silicone composite material may itself be used as various electrical and electronic parts or medical products such as bandages, or may be used in combination with various substrates such as metal substrates,

metal oxide substrates, glass substrates and plastic films. Additionally, because the silicone composite material of the present invention may have both an optically transparent portion and a reflective portion, the silicone composite material may be used as a portion of or an entire part for optical elements.

5 [0054]

[Optical semiconductor device]

The optical semiconductor device of the present invention will now be explained.

[0055] The optical semiconductor device according to the present invention is characterized by being manufacture by the above-described manufacturing method.

10 [0056] An example of such an optical semiconductor device of the present invention is a light-emitting diode (LED) (see FIGS. 1 to 4). In the optical semiconductor device of FIG. 1, a light reflection material 5 composed of cured silicone functions as a frame material (packaging material) of the optical semiconductor device, and a sealing agent 6 functions as a protectant of an optical semiconductor element 1. In the optical
15 semiconductor device of FIG. 2, a substrate 7 which has cured silicone functions as a substrate on which an optical semiconductor element 1 is mounted, and a sealing agent 6 functions as a protectant and a lens material of the optical semiconductor element 1. In the optical semiconductor device of FIG. 3, a dam material 8 composed of cured silicone controls outflow of a sealing agent 6 as frame material of the optical semiconductor device,
20 and the sealing agent 6 functions as a protectant of an optical semiconductor element 1. In the optical semiconductor device of FIG. 4, a fluorescent body-containing sheet composed of cured silicone converts the wavelength of light from an optical semiconductor element and diffuses light, and a sealing agent 6 functions as a protectant of the optical semiconductor element 1.

25 [0057] In the optical semiconductor device of the present invention, as illustrated in FIG. 1, an optical semiconductor element 1 is die bonded to a lead frame 2 by a die bonding material, and this optical semiconductor element 1 is wire bonded to lead frames 2, 3 by bonding wires 4, 4'. Around the periphery of this optical semiconductor element 1, with the exception of the upper part thereof, a light reflection material 5 composed of the
30 cured silicone is present. The optical semiconductor element 1 within this light reflection material 5 is sealed by the sealing agent 6.

[0058] The flow of manufacturing a surface mounted LED shown in FIG. 1 is exemplified by a method including the steps of: (1) forming the light reflection material 5

integrated with the lead frames 2, 3 by transfer molding, compression molding or injection molding a hydrosilylation reaction-curable silicone composition, (2) die bonding the optical semiconductor element 1 on the lead frame 2 using the die bonding material, (3) wire bonding the optical semiconductor element 1 and the lead frames 2, 3 using the bonding wires 4, 4', and (4) sealing the optical semiconductor element 1 using the sealing agent 6.

[0059] If the light reflection material is formed by the aforementioned transfer molding, compression molding or injection molding, the molding is preferably performed at a temperature of from 110°C to 170°C for from 60 to 300 seconds. Post curing may be performed for about 1 to 8 hours at a temperature of from 130°C to 180°C.

[0060] Furthermore, in another optical semiconductor device of the present invention, as illustrated in FIG. 2, an optical semiconductor element 1 is die bonded to a lead frame 2 by a die bonding material, and this optical semiconductor element 1 is wire bonded to lead frames 2, 3 by bonding wires 4, 4'. On a portion of the substrate 7 on which the optical semiconductor element 1 is mounted that contacts a sealing agent 6, the aforementioned cured silicone is present, and the optical semiconductor element 1 is sealed by the sealing agent 6.

[0061] The flow of manufacturing the surface mounted LED shown in FIG. 2 is exemplified by a method including the steps of: (1) forming the substrate 7 integrated with the lead frames 2, 3 by transfer molding, compression molding or injection molding the hydrosilylation reaction-curable silicone composition, (2) die bonding the optical semiconductor element 1 on the lead frame 2 using the die bonding material, (3) wire bonding the optical semiconductor element 1 and the lead frames 2, 3 using the bonding wires 4, 4', and (4) sealing the optical semiconductor element 1 using the sealing agent 6 composed of curable silicone composition.

[0062] Furthermore, in another optical semiconductor device of the present invention, as illustrated in FIG. 3, an optical semiconductor element 1 is die bonded to a lead frame 2 by a die bonding material, and this optical semiconductor element 1 is wire bonded to lead frames 2, 3 by bonding wires 4, 4'. Around the periphery of this optical semiconductor element 1, with the exception of the upper part thereof, a dam material 8 composed of cured silicone is present. The optical semiconductor element 1 within this dam material 8 is sealed by the sealing agent 6.

[0063] The flow of manufacturing the surface mounted LED shown in FIG. 3 is

exemplified by a method including the steps of: (1) die bonding the optical semiconductor element 1 on the lead frame 2 using the die bonding material, (2) wire bonding the optical semiconductor element 1 and the lead frames 2, 3 using the bonding wires 4, 4', (3) forming the dam material 8 around the periphery of the optical semiconductor element 1 on the substrate by dispensing a hydrosilylation reaction-curable silicone composition, and (4) sealing the optical semiconductor element 1 using the sealing agent 6 composed of a curable silicone composition.

[0064] Furthermore, in another optical semiconductor device of the present invention, as illustrated in FIG. 4, an optical semiconductor element 1 is die bonded to a lead frame 2 by a die bonding material, and this optical semiconductor element 1 is wire bonded to lead frames 2, 3 by bonding wires 4, 4'. This optical semiconductor element 1 is covered by a fluorescent substance-containing sheet 10 composed of cured silicone, and this fluorescent substance-containing sheet 10 and the optical semiconductor element 1 are sealed by the sealing agent 6.

[0065] The flow of manufacturing the surface mounted LED shown in FIG. 4 is exemplified by a method including the steps of: (1) forming a frame material 9 integrated with the lead frames 2, 3 by transfer molding, compression molding or injection molding a hydrosilylation reaction-curable silicone composition, (2) die bonding the optical semiconductor element 1 on the lead frame 2 using the die bonding material, (3) wire bonding the optical semiconductor element 1 and the lead frames 2, 3 using the bonding wires 4, 4', (4) covering the optical semiconductor element 1 with the fluorescent substance-containing sheet 10, and (5) filling the optical semiconductor element 1 and the fluorescent body-containing sheet 10 with the sealing agent 6 composed of a curable silicone composition.

[0066] The curing temperature of the sealing agent 6 is not particularly limited, but good curing is generally able to be obtained from room temperature to 220°C. Curing at a temperature from 60°C to 180°C is preferable, and curing at a temperature from 80°C to 150°C is more preferable, because it results in strong adhesion between the silicone layer and substrate. Furthermore, step curing is preferable, wherein the composite is heated at from room temperature to 100°C, preferably from 60°C to 80°C, and is then heated at from 80°C to 180°C, preferably from 100°C to 150°C, because adhesion between the silicone layer and substrate is further improved in some cases.

Examples

[0067] The method of manufacturing an optical semiconductor device and the optical semiconductor device of the present invention will now be described in detail using Examples. Furthermore, the curability and storage stability of the curable silicone composition, and the heat resistance of the cured silicone thereof were evaluated by the following methods.

[0068]

[(1) Evaluation of curability of curable silicone composition]

The light reflection material 5 (cured silicone) illustrated in FIG. 1 was produced by molding a hydrosilylation reaction-curable silicone composition integrated with lead frames 2, 3 at 150°C using a transfer molder. After the light reflection material was post-cured for 3 hours at 130°C, it was filled by dispensing the prescribed curable silicone composition to form the sealing agent 6. With the light reflection material filled with the curable silicone composition, curing of the curable silicone composition was begun at 150°C. The surface tack of the cured sealing agent 6 was checked at 5, 10, 30, 60, and 120 minutes after the start of curing, and the time until there was no tackiness was taken to be the curing time.

[0069]

[(2) Evaluation of long-term storability of curable silicone composition]

The viscosity of the curable silicone composition immediately after preparation was measured with a shear rate of 20 (1/sec) using a rheometer (AR550, manufactured by TA Instruments Corp.). After the composition was prepared and then left to stand for 24 hours at 25°C, the viscosity was measured by the same method and compared with the initial viscosity.

[0070]

[(3) Evaluation of heat resistance of cured silicone of curable silicone composition]

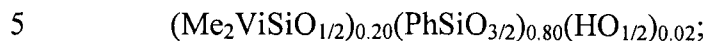
The produced optical semiconductor device was left for 20 minutes in a 300°C oven, and the degree of discoloration of the sealing agent was checked visually.

[0071] The cured silicones and sealing agents using in each of Practical Examples and Comparative Examples will now be specifically described. Note that in the formulae, Me, Ph, Vi, and Ep represent a methyl group, a phenyl group, a vinyl group, and a 3-glycidoxypentyl group, respectively.

[0072]

[Production Example 1 - Preparation of curable silicone composition 1 which forms cured silicone]

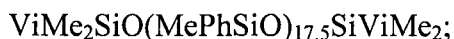
100.0 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



8.0 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:



20.0 parts by mass of a dimethylvinylsiloxy-terminated methylphenylpolysiloxane
10 represented by the average formula:

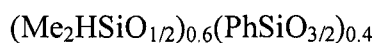


35.0 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



15 (amount resulting in 0.76 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and dimethylvinylsiloxy-terminated methylphenylpolysiloxane.);

7.5 parts by mass of a silicon-bonded hydrogen atom-containing methylphenylpolysiloxane
20 represented by the average unit formula:



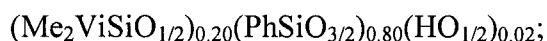
(amount resulting in 0.18 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and dimethylvinylsiloxy-terminated methylphenylpolysiloxane.); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution
25 of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (in an amount such that ing in 5 ppm by mass of the platinum metal in the present composition); 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition); 110 parts by mass of titanium oxide having 0.2 μm average primary particle diameter (SX-3103,
30 manufactured by Sakai Chemical Industry Co., Ltd.); 100 parts by mass of crushed quartz powder having 5 μm average particle diameter (SILICIC SAB-500, manufactured by Yamamori Tsuchimoto Mining Co., Ltd.); and 180 parts by mass of spherical silica having 15 μm average particle diameter (HS-202, manufactured by Nippon Steel & Sumikin

Materials Co., Ltd.) were homogeneously blended to prepare curable silicone composition 1.

[0073]

[Production Example 2 - Preparation of curable silicone composition 2 which forms cured
5 silicone]

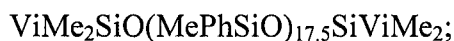
100.0 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



8.0 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by
10 the formula:



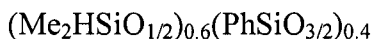
20.0 parts by mass of a dimethylvinylsiloxy-terminated methylphenylpolysiloxane represented by the average formula:



35.0 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the
15 formula:



(amount resulting in 0.76 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane,
20 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and dimethylvinylsiloxy-terminated methylphenylpolysiloxane); 7.5 parts by mass of a silicon-bonded hydrogen atom-containing methylphenylpolysiloxane represented by the average unit formula:



(amount resulting in 0.18 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane,
25 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and dimethylvinylsiloxy-terminated methylphenylpolysiloxane); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (amount resulting in 10 ppm by mass of the platinum metal in the present composition); 1-ethynyl-1-cyclohexanol

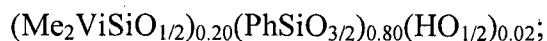
30 (amount resulting in 250 ppm by mass in the present composition); 110 parts by mass of titanium oxide having 0.2 μm average primary particle diameter (SX-3103, manufactured by Sakai Chemical Industry Co., Ltd.); 100 parts by mass of crushed quartz powder having 5 μm average particle diameter (SILICIC SAB-500, manufactured by Yamamori

Tsuchimoto Mining Co., Ltd.); and 180 parts by mass of spherical silica having 15 μm average particle diameter (HS-202, manufactured by Nippon Steel & Sumikin Materials Co., Ltd.) were homogeneously blended to prepare curable silicone composition 2.

[0074]

- 5 [Production Example 3 - Preparation of curable silicone composition 3 which forms cured silicone]

100.0 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



- 10 8.0 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:



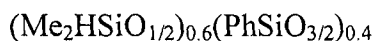
20.0 parts by mass of a dimethylvinylsiloxy-terminated methylphenylpolysiloxane represented by the average formula:

- 15 $\text{ViMe}_2\text{SiO}(\text{MePhSiO})_{17.5}\text{SiViMe}_2;$

35.0 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



- 20 (amount resulting in 0.76 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and dimethylvinylsiloxy-terminated methylphenylpolysiloxane); 7.5 parts by mass of a silicon-bonded hydrogen atom-containing methylphenylpolysiloxane represented by the average unit formula:

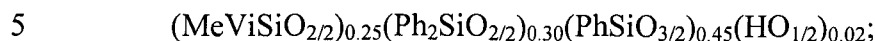


- 25 (amount resulting in 0.18 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, and dimethylvinylsiloxy-terminated methylphenylpolysiloxane); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (amount resulting in 10 ppm by mass of the platinum metal in the present composition); and 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition) were homogeneously blended to prepare curable silicone composition 3.

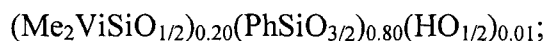
[0075]

[Production Example 4 - Preparation of curable silicone composition 4 which forms cured silicone]

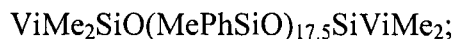
48.4 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



51.6 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



12.9 parts by mass of a dimethylvinylsiloxy-terminated methylphenylpolysiloxane represented by the average formula:



29.0 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:

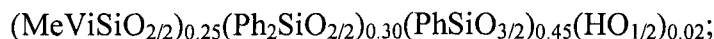


(amount resulting in 0.94 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxanes and dimethylvinylsiloxy-terminated methylphenylpolysiloxane); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (amount resulting in 5 ppm by mass of the platinum metal in the present composition); 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition); 118 parts by mass of titanium oxide having 0.2 μm average primary particle diameter (SX-3103, manufactured by Sakai Chemical Industry Co., Ltd.); and 213 parts by mass of spherical silica having 15 μm average particle diameter (HS-202, manufactured by Nippon Steel & Sumikin Materials Co., Ltd.) were homogeneously blended to prepare curable silicone composition 4.

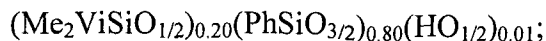
[0076]

[Production Example 5 - Preparation of curable silicone composition 5 which forms cured silicone]

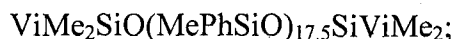
48.4 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



51.6 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



12.9 parts by mass of a dimethylvinylsiloxo-terminated methylphenylpolysiloxane represented by the average formula:



5 29.0 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



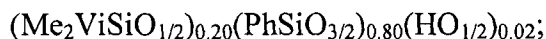
(amount resulting in 0.94 mol of silicon atom-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned

10 methylvinylphenylpolysiloxanes and dimethylvinylsiloxo-terminated methylphenylpolysiloxane); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (amount resulting in 10 ppm by mass of the platinum metal in the present composition); 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition); 118 parts by mass of titanium
15 oxide having 0.2 μm average primary particle diameter (SX-3103, manufactured by Sakai Chemical Industry Co., Ltd.); and 213 parts by mass of spherical silica having 15 μm average particle diameter (HS-202, manufactured by Nippon Steel & Sumikin Materials Co., Ltd.) were homogeneously blended to prepare curable silicone composition 5.

[0077]

20 [Production Example 6 - Preparation of curable silicone composition 6 as sealing agent]

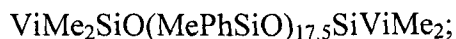
100 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



0.35 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented
25 by the formula:



30.4 parts by mass of a dimethylvinylsiloxo-terminated methylphenylpolysiloxane represented by the average formula:



30 4.17 parts by mass of an epoxy group-containing polysiloxane represented by the average unit formula:

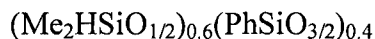


34.7 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the

formula:



(amount resulting in 1.03 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxyl-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); and 4.17 parts by mass of a silicon-bonded hydrogen-containing methylphenylpolysiloxane represented by the average unit formula:

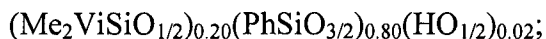


(amount resulting in 0.14 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxyl-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane) were homogeneously blended to obtain curable silicone composition 6 having viscosity of 2,400 mPa·s. After the curable silicone composition 6 was left to stand for 24 hours at 25°C, its viscosity was 2,400 mPa·s.

[0078]

[Production Example 7 - Preparation of curable silicone composition 7 as sealing agent]

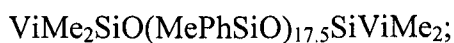
100 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



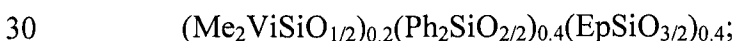
1.59 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:



21.4 parts by mass of a dimethylvinylsiloxyl-terminated methylphenylpolysiloxane represented by the average formula:



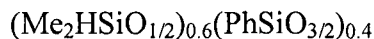
3.94 parts by mass of an epoxy group-containing polysiloxane represented by the average unit formula:



28.7 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



(amount resulting in 0.82 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxo-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); and 3.44 parts by mass of a silicon-bonded hydrogen-containing methylphenylpolysiloxane represented by the average unit formula:

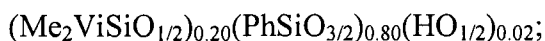


(amount resulting in 0.11 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxo-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane) were homogeneously blended to obtain curable silicone composition 7 having viscosity of 4,600 mPa·s. After the curable silicone composition 7 was left to stand for 24 hours at 25°C, its viscosity was 4,600 mPa·s.

15 [0079]

[Production Example 8 - Preparation of curable silicone composition 8 as sealing agent]

100 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



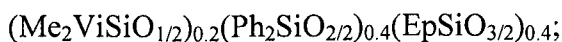
20 0.35 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:



30.4 parts by mass of a dimethylvinylsiloxo-terminated methylphenylpolysiloxane represented by the average formula:

25 $\text{ViMe}_2\text{SiO}(\text{MePhSiO})_{17.5}\text{SiViMe}_2;$

4.17 parts by mass of an epoxy group-containing polysiloxane represented by the average unit formula:



30 34.7 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



(amount resulting in 1.03 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane,

1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxyl-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); 4.17 parts by mass of a silicon-bonded hydrogen-containing methylphenylpolysiloxane represented by the average unit formula:

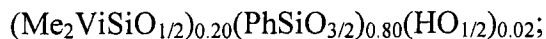


(amount resulting in 0.14 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxyl-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); and 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition) were homogeneously mixed to obtain curable silicone composition 8 having viscosity of 2,400 mPa·s. After the curable silicone composition 8 was left to stand for 24 hours at 25°C, its viscosity was 2,400 mPa·s.

[0080]

[Production Example 9 - Preparation of curable silicone composition 9 as sealing agent]

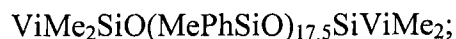
100 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



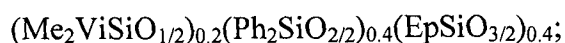
1.59 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:



21.4 parts by mass of a dimethylvinylsiloxyl-terminated methylphenylpolysiloxane represented by the average formula:



3.94 parts by mass of an epoxy group-containing polysiloxane represented by the average unit formula:

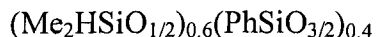


28.7 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



(amount resulting in 0.82 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxyl-terminated

methylphenylpolysiloxane, and epoxy group-containing polysiloxane); 3.44 parts by mass of a silicon-bonded hydrogen-containing methylphenylpolysiloxane represented by the average unit formula:

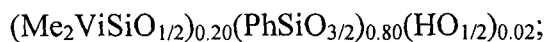


- 5 (amount resulting in 0.11 mol of silicon atom-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxy-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); and 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the
10 present composition) were homogeneously mixed to obtain curable silicone composition 9 having viscosity of 4,600 mPa·s. After the curable silicone composition 4 was left to stand for 24 hours at 25°C, its viscosity was 4,600 mPa·s.

[0081]

[Production Example 10 - Preparation of curable silicone composition 10 as sealing agent]

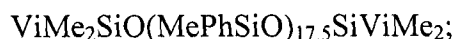
- 15 100 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



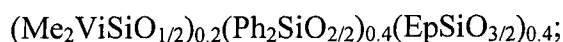
0.35 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:

- 20 $(\text{MeViSiO})_4;$

30.4 parts by mass of a dimethylvinylsiloxy-terminated methylphenylpolysiloxane represented by the average formula:



- 4.17 parts by mass of an epoxy group-containing polysiloxane represented by the average
25 unit formula:

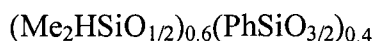


34.7 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



- 30 (amount resulting in 1.03 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxy-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); 4.17 parts by mass

of a silicon-bonded hydrogen-containing methylphenylpolysiloxane represented by the average unit formula:

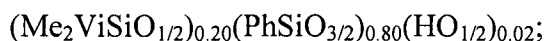


(amount resulting in 0.14 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxy-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (amount resulting in 5 ppm by mass of the platinum metal in the present composition); and 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition) were homogeneously mixed to obtain curable silicone composition 10 having viscosity of 2,400 mPa·s. After the curable silicone composition 10 was left to stand for 24 hours at 25°C, its viscosity was 5,800 mPa·s.

[0082]

[Production Example 11 - Preparation of curable silicone composition 11 as sealing agent]

100 parts by mass of a methylvinylphenylpolysiloxane represented by the average unit formula:



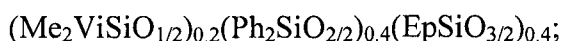
1.59 parts by mass of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane represented by the formula:



21.4 parts by mass of a dimethylvinylsiloxy-terminated methylphenylpolysiloxane represented by the average formula:



3.94 parts by mass of an epoxy group-containing polysiloxane represented by the average unit formula:

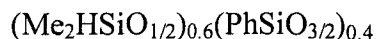


28.7 parts by mass of 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane represented by the formula:



(amount resulting in 0.82 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxy-terminated

methylphenylpolysiloxane, and epoxy group-containing polysiloxane); 3.44 parts by mass of a silicon-bonded hydrogen-containing methylphenylpolysiloxane represented by the average unit formula:



- 5 (amount resulting in 0.11 mol of silicon-bonded hydrogen atoms in this component relative to 1 mol of total vinyl groups in the aforementioned methylvinylphenylpolysiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, dimethylvinylsiloxyl-terminated methylphenylpolysiloxane, and epoxy group-containing polysiloxane); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of
10 platinum (amount resulting in 5 ppm by mass of the platinum metal in the present composition); and 1-ethynyl-1-cyclohexanol (amount resulting in 250 ppm by mass in the present composition) were homogeneously mixed to obtain curable silicone composition 11 having viscosity of 4,600 mPa·s. After the curable silicone composition 11 was left to stand for 24 hours at 25°C, its viscosity was 10,600 mPa·s.

15 [0083]

[Practical Example 1]

- The curable silicone composition 1 prepared in Production Example 1 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable
20 silicone composition 6 prepared in Production Example 6 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

25 [0084]

[Practical Example 2]

- The curable silicone composition 1 prepared in Production Example 1 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable
30 silicone composition 7 prepared in Production Example 7 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing

agent was checked visually. Results of the evaluation are shown in Table 1.

[0085]

[Practical Example 3]

The curable silicone composition 2 prepared in Production Example 2 was molded
5 integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a
150°C oven to obtain a light reflection material. This was filled by dispensing the curable
silicone composition 6 prepared in Production Example 6 and then curing was performed
for a prescribed time in a 150°C oven, and curability was assessed according to surface
tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat
10 resistance test was performed for 20 minutes. The degree of discoloration of the sealing
agent was checked visually. Results of the evaluation are shown in Table 1.

[0086]

[Practical Example 4]

The curable silicone composition 2 prepared in Production Example 2 was molded
15 integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a
150°C oven to obtain a light reflection material. This was filled by dispensing the curable
silicone composition 7 prepared in Production Example 7 and then curing was performed
for a prescribed time in a 150°C oven, and curability was assessed according to surface
tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat
20 resistance test was performed for 20 minutes. The degree of discoloration of the sealing
agent was checked visually. Results of the evaluation are shown in Table 1.

[0087]

[Practical Example 5]

The curable silicone composition 3 prepared in Production Example 3 was molded
25 integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a
150°C oven to obtain a light reflection material. This was filled by dispensing the curable
silicone composition 6 prepared in Production Example 6 and then curing was performed
for a prescribed time in a 150°C oven, and curability was assessed according to surface
tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat
30 resistance test was performed for 20 minutes. The degree of discoloration of the sealing
agent was checked visually. Results of the evaluation are shown in Table 1.

[0088]

[Practical Example 6]

The curable silicone composition 4 prepared in Production Example 4 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 6 prepared in Production Example 6 and then curing was performed
5 for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0089]

10 [Practical Example 7]

The curable silicone composition 4 prepared in Production Example 4 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 7 prepared in Production Example 7 and then curing was performed
15 for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0090]

20 [Practical Example 8]

The curable silicone composition 5 prepared in Production Example 5 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 6 prepared in Production Example 6 and then curing was performed
25 for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0091]

30 [Practical Example 9]

The curable silicone composition 5 prepared in Production Example 5 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable

silicone composition 7 prepared in Production Example 7 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0092]**[Practical Example 10]**

The curable silicone composition 1 prepared in Production Example 1 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 8 prepared in Production Example 8 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0093]**[Practical Example 11]**

The curable silicone composition 2 prepared in Production Example 2 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 9 prepared in Production Example 9 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0094]**[Comparative Example 1]**

The curable silicone composition 4 prepared in Production Example 4 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 10 prepared in Production Example 10 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a

heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.

[0095]

[Comparative Example 2]

- 5 The curable silicone composition 5 prepared in Production Example 5 was molded integrated with a lead frame for 2 minutes at 150°C, and then post-cured for 1 hour in a 150°C oven to obtain a light reflection material. This was filled by dispensing the curable silicone composition 11 prepared in Production Example 11 and then curing was performed for a prescribed time in a 150°C oven, and curability was assessed according to surface tack. The obtained optical semiconductor device was put in a 300°C oven, and a heat resistance test was performed for 20 minutes. The degree of discoloration of the sealing agent was checked visually. Results of the evaluation are shown in Table 1.
- 10

[0096]

[Table 1]

		Practical Example 1	Practical Example 2	Practical Example 3	Practical Example 4	Practical Example 5
Light reflection material	Production Example 1	○	○	—	—	—
	Production Example 2	—	—	○	○	—
	Production Example 3	—	—	—	—	○
	Production Example 4	—	—	—	—	—
	Production Example 5	—	—	—	—	—
Sealing agent	Production Example 6	○	—	○	—	○
	Production Example 7	—	○	—	○	—
	Production Example 8	—	—	—	—	—
	Production Example 9	—	—	—	—	—
	Production Example 10	—	—	—	—	—
	Production Example 11	—	—	—	—	—
Curability of sealing agent (150°C cured tack-free time)		30	30	10	10	10
Discoloration of sealing agent at 300°C x 10 minutes		No discoloration	No discoloration	No discoloration	No discoloration	No discoloration

[0097]

[Table 1] Continued

		Practical Example 6	Practical Example 7	Practical Example 8	Practical Example 9	Practical Example 10
Light reflection material	Production Example 1	—	—	—	—	○
	Production Example 2	—	—	—	—	—
	Production Example 3	—	—	—	—	—
	Production Example 4	○	○	—	—	—
	Production Example 5	—	—	○	○	—
Sealing agent	Production Example 6	○	—	○	—	—
	Production Example 7	—	○	—	○	—
	Production Example 8	—	—	—	—	○
	Production Example 9	—	—	—	—	—
	Production Example 10	—	—	—	—	—
	Production Example 11	—	—	—	—	—
Curability of sealing agent (150°C cured tack- free time)		30	30	10	10	120
Discoloration of sealing agent at 300°C x 10 minutes		No discoloration	No discoloration	No discoloration	No discoloration	No discoloration

[0098] [Table 1] Continued

		Practical Example 11	Comparative Example 1	Comparative Example 2
Light reflection material	Production Example 1	—	—	—
	Production Example 2	○	—	—
	Production Example 3	—	—	—
	Production Example 4	—	○	—
	Production Example 5	—	—	○
Sealing agent	Production Example 6	—	—	○
	Production Example 7	—	—	—
	Production Example 8	—	—	—
	Production Example 9	○	—	—
	Production Example 10	—	○	—
	Production Example 11	—	—	○
Curability of sealing agent (150°C cured tack- free time)		120	5	5
Discoloration of sealing agent at 300°C x 10 minutes		No discoloration	Yellowed	Yellowed

[0099] From the results shown in Table 1 it is seen that Practical Examples 1 to 11 exhibit results superior to those of Comparative Examples 1 and 2 with regard to

- 5 discoloration of the sealing agent. As a result, in the optical semiconductor devices pertaining to the Practical Examples produced by the method of the present invention, discoloration at high, temperature caused by the hydrosilylation reaction catalyst can be inhibited, and also, because the curable silicone composition curing reaction itself is effectively performed by the hydrosilylation reaction catalyst in the cured silicone that
- 10 contacts the sealing agent, a sealing agent that assures the desired heat resistance and storage stability can be formed.

Industrial Applicability

[0100] According to the present invention, a method of manufacturing an optical semiconductor device of which the sealing agent realizes storage stability, has good heat

15 resistance, and can greatly resist discoloration can be provided; and an optical semiconductor device obtained by the manufacturing method can be provided.

Description of Symbols**[0101]**

- | | | |
|----|-------|---|
| | 1 | Optical semiconductor element |
| | 2 | Lead frame |
| 5 | 3 | Lead frame |
| | 4, 4' | Bonding wire |
| | 5 | Light reflection material composed of cured silicone |
| | 6 | Sealing agent |
| | 7 | Substrate having cured silicone |
| 10 | 8 | Dam material composed of cured silicone |
| | 9 | Frame material |
| | 10 | Fluorescent substance-containing sheet composed of cured silicone |

CLAIMS

1. A method of manufacturing an optical semiconductor device comprising:
a step of sealing an optical semiconductor element using a curable silicone
composition; the curable silicone composition, although cured by a hydrosilylation
5 reaction, being hydrosilylation reaction catalyst free or, if containing a hydrosilylation
reaction catalyst, a content of the hydrosilylation reaction catalyst being insufficient to
cure the composition; and
the optical semiconductor element being sealed in a state in which the curable silicone
composition contacts a cured silicone that contains a hydrosilylation reaction catalyst.
- 10 2. The method of manufacturing an optical semiconductor device according to
claim 1, wherein the curable silicone composition comprises:
(A) at least one type of organopolysiloxane having not less than two silicon-bonded
alkenyl groups per molecule; and
(B) at least one type of organopolysiloxane having not less than two silicon-bonded
15 hydrogen atoms per molecule,
and is hydrosilylation reaction catalyst free, or, if contains a hydrosilylation reaction
catalyst, a content of a hydrosilylation reaction catalyst is insufficient to cure the
composition.
3. The method of manufacturing an optical semiconductor device according to
20 claim 1 or 2, wherein the cured silicone is a light reflection material, a substrate, a dam
material, or a fluorescent body-containing sheet.
4. The method of manufacturing an optical semiconductor device according to any
one of claims 1 to 3, wherein the hydrosilylation reaction catalyst is a platinum-based
catalyst.
- 25 5. The method of manufacturing an optical semiconductor device according to any
one of claims 1 to 4, wherein the curable silicone composition does not contain a
hydrosilylation reaction inhibitor.
6. The method of manufacturing an optical semiconductor device according to any
one of claims 1 to 5, wherein the cured silicone contains at least one type of white
30 pigment selected from the group consisting of titanium oxide, zinc oxide, barium
titanate, barium sulfate, and zirconium oxide.

7. The method of manufacturing an optical semiconductor device according to any one of claims 1 to 6, wherein the cured silicone contains at least one type of inorganic filler selected from the group consisting of non-spherical silica, spherical silica, and glass fibers.
- 5 8. An optical semiconductor device manufactured by the manufacturing method described in any one of claims 1 to 7.

FIG. 1

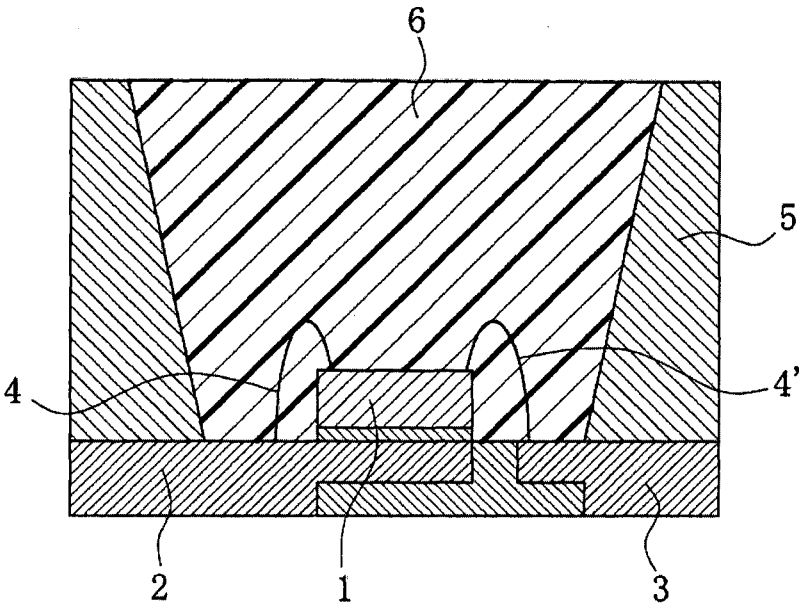


FIG. 2

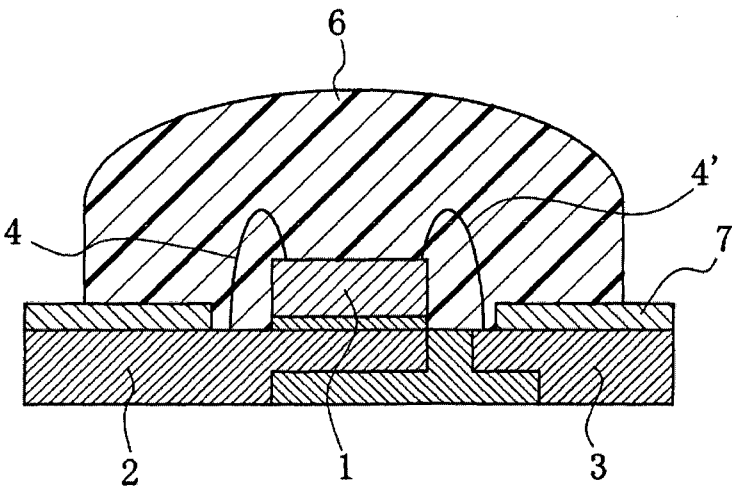


FIG. 3

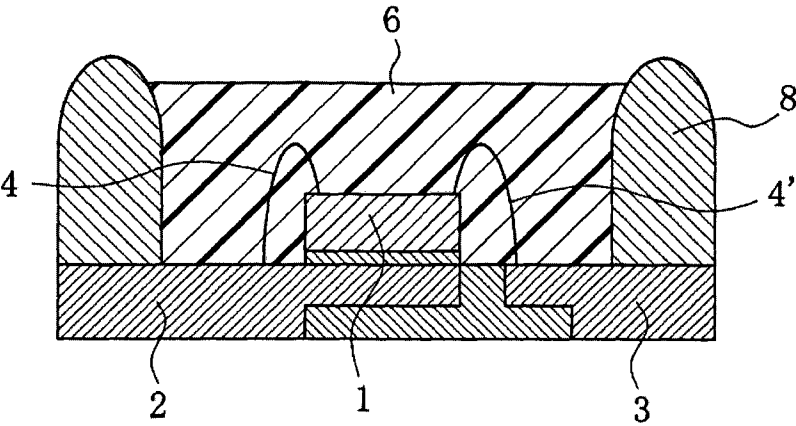
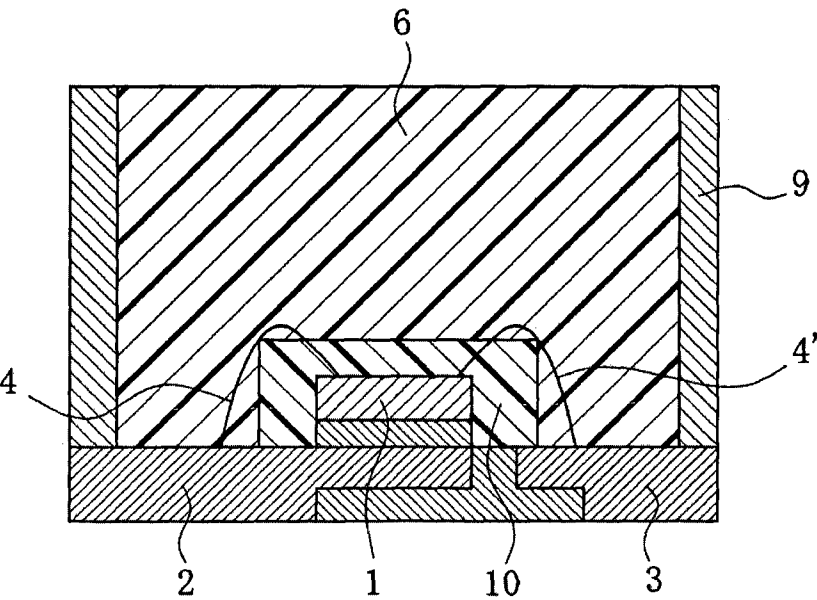


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/073592

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. H01L33/56 (2010.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H01L33/00-33/64

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2014
 Registered utility model specifications of Japan 1996-2014
 Published registered utility model applications of Japan 1994-2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-70719 A (Nitto Denko Corporation) 2010.04.02, [0003] [0007] [0028] & US 2010/0075158 A1 & EP 2166031 A1 & CN 101684198 A & KR 10-2010-0033927 A	1-8
A	JP 2009-24117 A (Sony Corporation) 2009.02.05, [0036] [0154] (Family: none)	1-8
A	JP 2009-203475 A (Mitsubishi Chemical Corporation) 2009.09.10, the whole document and figures & US 2009/0218592 A1 & US 2009/0221783 A1	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

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“&” document member of the same patent family

Date of the actual completion of the international search

17.11.2014

Date of mailing of the international search report

02.12.2014

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