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- (71) Applicant: **DOW CORNING TORAY CO., LTD.**
[JP/JP]; 5-1, Otemachi 1-chome, Chiyoda-ku, Tokyo,
1000004 (JP).
- (72) Inventors: **SUTO, Michitaka**; c/o Dow Corning Toray
Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba,
2990108 (JP). **NISHIJIMA, Kazuhiro**; c/o Dow Corning
Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba,
2990108 (JP). **IIMURA, Tomohiro**; c/o Dow Corning
Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba,
2990108 (JP). **FURUKAWA, Haruhiko**; c/o Dow Corning
Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba,
2990108 (JP). **MORITA, Yoshitsugu**; c/o Dow
Corning Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi,
Chiba, 2990108 (JP).

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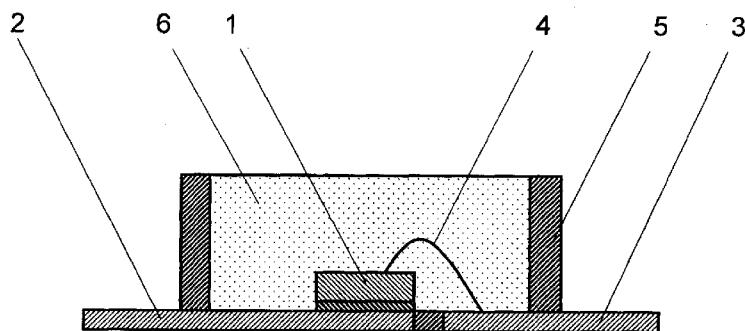
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(54) Title: CURABLE SILICONE COMPOSITION, CURED PRODUCT THEREOF, AND OPTICAL SEMICONDUCTOR
DEVICE

Figure 1



(57) Abstract: The present invention relates to a curable silicone composition comprising: (A) an alkenyl group-containing organo-
polysiloxane having a condensed polycyclic aromatic group or a group containing a condensed polycyclic aromatic group; (B) an or-
ganopolysiloxane resin having at least two alkenyl groups in a molecule; (C) an organosiloxane (C₁) having silicon-bonded hydro-
gen atoms at both molecular terminals, an organopolysiloxane (C₂) having at least two silicon-bonded hydrogen atoms in a molecule,
or a mixture of components (C₁) and (C₂); and (D) a hydrosilylation reaction catalyst. The curable silicone composition has excellent
handleability and can form a cured product with a high refractive index and low gas permeability.



DESCRIPTION**CURABLE SILICONE COMPOSITION, CURED PRODUCT THEREOF,
AND OPTICAL SEMICONDUCTOR DEVICE****Technical Field**

5 **[0001]** The present invention relates to a curable silicone composition, a cured product formed by curing the composition, and an optical semiconductor device produced using the composition.

[0002] Priority is claimed on Japanese Patent Application No. 2012-288121, filed on December 28, 2012, the content of which is incorporated herein by reference.

10 **Background Art**

[0003] Curable silicone compositions are used as sealing materials or protective coating materials for optical semiconductor elements in optical semiconductor devices such as light emitting diodes (LEDs). However, cured products of curable silicone compositions exhibit high gas permeability, when such cured products are used in high
15 brightness LEDs, which exhibit high light intensity and generate large amounts of heat, problems occur such as discoloration of the sealing material due to corrosive gases and a reduction in brightness due to corrosion of silver plated on the LED substrate.

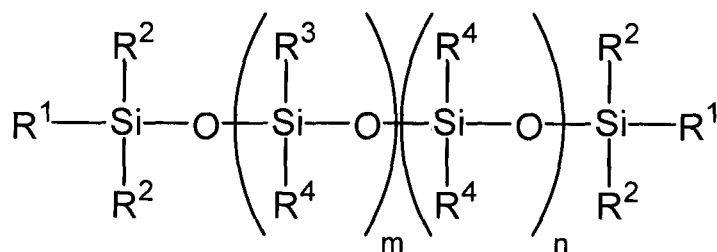
[0004] Therefore, a curable silicone composition which forms a cured product with low gas permeability is proposed in Japanese Unexamined Patent Application Publication
20 No. 2012-052045A, but such a curable silicone composition is problematic in that the viscosity is high, the handleability is poor, and the gas permeability of the cured product thereof is not sufficiently low.

[0005] An object of the present invention is to provide a curable silicone composition having excellent handleability and forming a cured product with a high refractive index
25 and low gas permeability. In addition, another object of the present invention is to provide a cured product having a high refractive index and a low gas permeability and to provide an optical semiconductor device having excellent reliability.

Disclosure of Invention

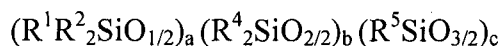
[0006] The curable silicone composition of the present invention comprises:

30 (A) an organopolysiloxane represented by the general formula:



wherein R^1 are the same or different, and are each an alkenyl group having from 2 to 12 carbon atoms; R^2 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms; R^3 is a condensed polycyclic aromatic group or a group containing a condensed polycyclic aromatic group; R^4 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; and m is an integer from 1 to 100, n is an integer from 0 to 100, where $1 \leq m + n \leq 100$;

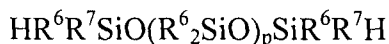
(B) an organopolysiloxane resin represented by the average unit formula:



wherein R^1 , R^2 , and R^4 are synonymous with those described above; R^5 is an aryl group having from 6 to 20 carbon atoms or an aralkyl group having from 7 to 20 carbon atoms; and a , b , and c are respectively numbers satisfying $0.01 \leq a \leq 0.5$, $0 \leq b \leq 0.7$, $0.1 \leq c < 0.9$, and $a + b + c = 1$;

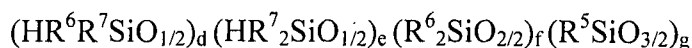
and having at least two alkenyl groups in a molecule, in an amount of 10 to 80 mass % of the composition;

(C) an organosiloxane (C_1) represented by the general formula:



wherein R^6 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms; R^7 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms; and p is an integer from 0 to 100;

an organopolysiloxane (C_2) having at least two silicon-bonded hydrogen atoms in a molecule and represented by the average unit formula:



wherein R^5 , R^6 , and R^7 are synonymous with those described above; and d , e , f , and g are numbers that satisfy such that $0.01 \leq d \leq 0.7$, $0 \leq e \leq 0.5$, $0 \leq f \leq 0.7$,

$0.1 \leq g < 0.9$, and $d + e + f + g = 1$; or

a mixture of component (C_1) and component (C_2), in an amount such that the number of silicon-bonded hydrogen atoms in the present component is from 0.1 to 5 moles per 1 mol of total alkenyl groups in components (A) and (B); and

(D) an effective amount of a hydrosilylation reaction catalyst.

[0007] The cured product of the present invention is formed by curing the aforementioned curable silicone composition.

10 [0008] The optical semiconductor device of the present invention is produced by sealing an optical semiconductor element with a cured product of the curable silicone composition described above.

Effects of Invention

15 [0009] The curable silicone composition of the present invention has excellent handleability and forms a cured product with a high refractive index and low gas permeability. Furthermore, the cured product of the present invention is characterized by having a high refractive index and a low gas permeability, and the optical semiconductor device of the present invention is characterized by exhibiting excellent reliability.

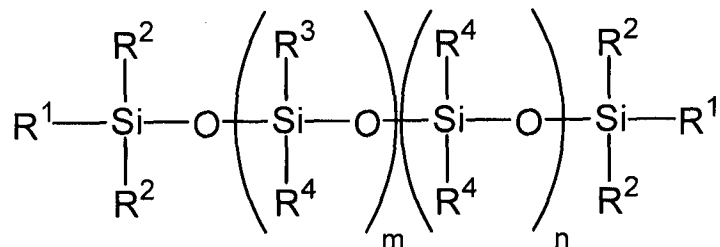
Brief Description of the Drawings

20 [0010] Figure 1 is a cross-sectional view of an LED serving as an example of the optical semiconductor device of the present invention.

Detailed Description of the Invention

[0011] First, the curable silicone composition of the present invention will be described in detail.

25 [0012] Component (A) is a base compound of this composition and is an organopolysiloxane represented by the general formula:



[0013] In the formula, R^1 are the same or different, and are each an alkenyl group having from 2 to 12 carbon atoms, examples of which include vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, heptenyl groups, octenyl groups, nonenyl groups, decenyl groups, undecenyl groups, and dodecenyl groups, and a vinyl group is preferable.

[0014] In the formula, R^2 are the same or different, and are each an alkyl group having from 1 to 12 carbons, an alkenyl group having from 2 to 12 carbons, an aryl group having from 6 to 20 carbons, or an aralkyl group having from 7 to 20 carbons. Examples of the alkyl group of R^2 include methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, and dodecyl groups, and a methyl group is preferable. Examples of the alkenyl group of R^2 include the same groups described for R^1 . Examples of the aryl groups of R^2 include phenyl groups, tolyl groups, xylyl groups, naphthyl groups, anthracenyl groups, phenanthryl groups, pyrenyl groups, and groups in which the hydrogen atoms of these aryl groups are substituted with alkyl groups such as methyl groups and ethyl groups; alkoxy groups such as methoxy groups and ethoxy groups; or halogen atoms such as chlorine atoms and bromine atoms. Of these, phenyl groups and naphthyl groups are preferable. Examples of the aralkyl groups of R^2 include benzyl groups, phenethyl groups, naphthyl ethyl groups, naphthyl propyl groups, anthracenyl ethyl groups, phenanthryl ethyl groups, pyrenyl ethyl groups, and groups in which the hydrogen atoms of these aralkyl groups are substituted with alkyl groups such as methyl groups and ethyl groups; alkoxy groups such as methoxy groups and ethoxy groups; or halogen atoms such as chlorine atoms and bromine atoms.

[0015] In the formula, R^3 is a condensed polycyclic aromatic group or a group including a condensed polycyclic aromatic group. Examples of the condensed polycyclic aromatic group of R^3 include a naphthyl group, an anthracenyl group, a phenanthryl group, a pyrenyl group, and such condensed polycyclic aromatic groups where a hydrogen atom is replaced by an alkyl group such as a methyl group, an ethyl group, and the like; by an alkoxy group such as a methoxy group, an ethoxy group, and the like; or by a halogen atom such as a chlorine atom, a bromine atom, and the like. Of these, the naphthyl group is preferable. Examples of the group containing a condensed polycyclic aromatic group of R^3 include condensed polycyclic aromatic group-containing alkyl groups such as naphthyl ethyl groups, naphthyl propyl groups, anthracenyl ethyl groups, phenanthryl ethyl

groups, and pyrenyl ethyl groups and such condensed polycyclic aromatic groups in which a hydrogen atom is substituted with an alkyl group such as a methyl group or an ethyl group; an alkoxy group such as a methoxy group or an ethoxy group, or a halogen atom such as a chlorine atom or a bromine atom.

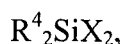
5 [0016] In the formula, R^4 are the same or different, and are alkyl groups having from 1 to 12 carbons, alkenyl groups having from 2 to 12 carbons, or phenyl groups. Examples of the alkyl group of R^4 include the same alkyl groups described for R^2 . Examples of the alkenyl group of R^4 include the same groups described for R^1 .

[0017] In the formula, m is an integer in a range from 1 to 100, and n is an integer in a range from 0 to 100, where $1 \leq m + n \leq 100$. Preferably, m is an integer in a range from 1 to 50, and n is an integer in a range from 0 to 30. More preferably, m is an integer in a range from 1 to 25, and n is an integer in a range from 0 to 10. This is because when m is greater than or equal to the lower limit of the aforementioned range, it is possible to impart the cured product with sufficient gas barrier properties, and when m is less than or equal to the upper limit of the aforementioned range, the handleability of the resulting composition improves.

[0018] The method for preparing the organopolysiloxane of such component (A) is not particularly limited, but an example is a method of performing a hydrolysis/condensation reaction on a silane compound (I-1) represented by the general formula:



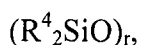
a silane compound (I-2) represented by the general formula:



a cyclic siloxane compound (II-1) represented by the general formula:



25 and a cyclic siloxane compound (II-2) represented by the general formula:



or a straight-chain organosiloxane (III-1) represented by the general formula:



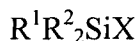
a straight-chain organosiloxane (III-2) represented by the general formula:



a disiloxane (IV-2) represented by the general formula:



and/or a silane compound (IV-2) represented by the general formula:



in the presence of an acid or an alkali.

- 5 **[0019]** In the formula, R^1 is an alkenyl group having from 2 to 12 carbon atoms, examples of which are the same groups as those described above. In the formulas, R^2 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms, examples of which are the same groups as those described above. In the formulas, R^3 is a condensed polycyclic aromatic group or a group containing a condensed polycyclic aromatic group, examples of which are the same groups as those described above. In the formulas, R^4 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, examples of which are the same groups as those described above. In the formula, r is an integer of 1 or higher, and s is an integer of 2 or higher. In the formulas, X is an alkoxy group such as a methoxy group, an ethoxy group, or a propoxy group; an acyloxy group such as an acetoxy group; a halogen atom such as a chlorine atom or a bromine atom; or a hydroxyl group.

- 15 **[0020]** Examples of such silane compounds (I-1) and (I-2) include alkoxysilanes such as phenylmethyldimethoxysilane, naphthylmethyldimethoxysilane, anthracenylmethyldimethoxysilane, phenanthrylmethyldimethoxysilane, pyrenylmethyldimethoxysilane, phenylethyldimethoxysilane, naphthylethyldimethoxysilane, anthracenylethyldimethoxysilane, phenanthrylethyldimethoxysilane, pyrenylethyldimethoxysilane, phenylmethyldiethoxysilane, naphthylmethyldiethoxysilane, anthracenylmethyldiethoxysilane, phenantrylmethyldiethoxysilane, pyrenylmethyldiethoxysilane, phenylethyldiethoxysilane, naphthylethyldiethoxysilane, anthracenylethyldiethoxysilane, phenanthrylethyldiethoxysilane, pyrenylethyldiethoxysilane, diphenyldimethoxysilane, naphthylphenyldimethoxysilane, anthracenylphenyldimethoxysilane, phenanthrylphenyldimethoxysilane, pyrenylphenyldimethoxysilane, diphenyldiethoxysilane, naphthylphenyldiethoxysilane, anthracenylphenyldiethoxysilane, phenanthrylphenyldiethoxysilane, and pyrenylphenyldiethoxysilane; halosilanes such as phenylmethyldichlorosilane,

naphthylmethyldichlorosilane, anthracenylmethyldichlorosilane, phenanthrylmethyldichlorosilane, pyrenylmethyldichlorosilane, phenylethyldichlorosilane, naphthylethyldichlorosilane, anthracenylethyldichlorosilane, phenanthrylethyldichlorosilane, pyrenylethyldichlorosilane, diphenyldichlorosilane, naphthylphenyldichlorosilane, anthracenylphenyldichlorosilane, phenanthrylphenyldichlorosilane, and pyrenylphenyldichlorosilane; and hydroxysilanes such as phenylmethyldihydroxysilane, naphthylmethyldihydroxysilane, anthracenylmethyldihydroxysilane, phenanthrylmethyldihydroxysilane, pyrenylmethyldihydroxysilane, diphenyldihydroxysilane, naphthylphenyldihydroxysilane, anthracenylphenyldihydroxysilane, phenanthrylphenyldihydroxysilane, and pyrenylphenyldihydroxysilane.

[0021] In addition, examples of the cyclic siloxane compounds (II-1) and (II-2) include cyclic silicones such as cyclic phenylmethylsiloxane, cyclic diphenylsiloxane, cyclic naphthylmethylsiloxane, cyclic naphthylphenylsiloxane, cyclic anthracenylmethylsiloxane, cyclic anthracenylphenylsiloxane, cyclic phenanthrylmethylsiloxane, and cyclic phenanthrylphenylsiloxane.

[0022] In addition, examples of the straight-chain organosiloxanes (III-1) and (III-2) include polysiloxanes capped at both molecular terminals with silanol groups such as phenylmethylpolysiloxanes capped at both molecular terminals with silanol groups, diphenylpolysiloxanes capped at both molecular terminals with silanol groups, naphthylmethylpolysiloxanes capped at both molecular terminals with silanol groups, naphthylphenylpolysiloxanes capped at both molecular terminals with silanol groups, anthracenylmethylpolysiloxanes capped at both molecular terminals with silanol groups, anthracenylphenylpolysiloxanes capped at both molecular terminals with silanol groups, phenanthrylmethylpolysiloxanes capped at both molecular terminals with silanol groups, and phenanthrylphenylpolysiloxanes capped at both molecular terminals with silanol groups.

[0023] Examples of the disiloxane (IV-1) include 1,3-dimethyl-1,3-diphenyl-1,3-divinylsiloxane, 1,3-dimethyl-1,3-diphenyl-1,3-diallyldisiloxane, 1,1,3,3-tetraphenyl-1,3-divinyldisiloxane, and 1,1,3,3-tetraphenyl-1,3-diallyldisiloxane.

[0024] Examples of the silane compound (IV-2) include alkoxysilanes such as vinylmethylphenylmethoxysilane, vinyl-diphenylmethoxysilane, allylmethylphenylmethoxysilane, and allyl-diphenylmethoxysilane; acetoxysilanes such as

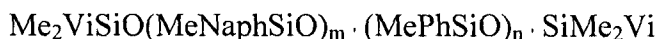
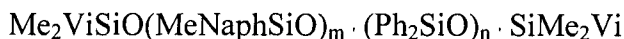
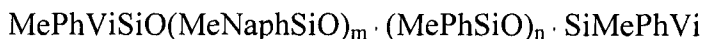
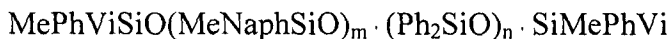
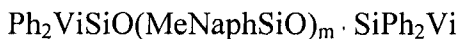
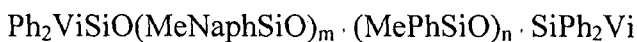
vinylmethylphenylacetoxysilane, allylmethylphenylacetoxysilane, vinyl-diphenylacetoxysilane, and allyldiphenylacetoxysilane; halosilanes such as vinylmethylphenylchlorosilane, allylmethylphenylchlorosilane, vinyl-diphenylchlorosilane, allyldiphenylchlorosilane; and hydroxysilanes such as vinylmethylphenylhydroxysilane, allylmethylphenylhydroxysilane, vinyl-diphenylhydroxysilane, and allyldiphenylhydroxysilane.

[0025] Examples of acids that can be used include hydrochloric acid, acetic acid, formic acid, nitric acid, oxalic acid, sulfuric acid, phosphoric acid, polyphosphoric acid, polyvalent carboxylic acid, trifluoromethanesulfonic acid, and ion exchange resins.

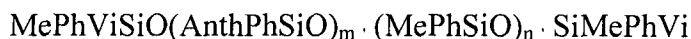
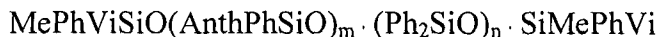
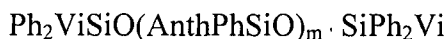
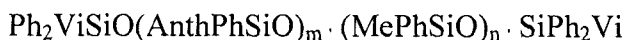
10 **[0026]** Examples of alkalis that can be used include hydroxides such as sodium hydroxide and potassium hydroxide; oxides such as magnesium oxide and calcium oxide; and hydrogen halide scavengers such as triethylamine, diethylamine, ammonia, picoline, pyridine, and 1,8-bis(dimethylamino)naphthalene.

[0027] In the preparation method described above, an organic solvent may be used.
15 Examples of organic solvents that can be used include aromatic or aliphatic hydrocarbons and mixtures of two or more types thereof. Examples of preferable organic solvents include toluene and xylene.

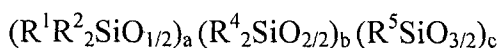
[0028] Examples of such component (A) include the following organopolysiloxanes. In the formulas, Me, Vi, Ph, Naph, and Anth respectively represent a methyl group, a vinyl group, a phenyl group, a naphthyl group, and an anthracenyl groups, **m'** is an integer from
20 1 to 100, and **n'** is an integer from 1 to 100.



- $\text{Ph}_2\text{ViSiO}(\text{MeNaphSiO})_m \cdot (\text{Ph}_2\text{SiO})_n \cdot \text{SiPh}_2\text{Vi}$
- $\text{Me}_2\text{ViSiO}(\text{NaphPhSiO})_m \cdot \text{SiMe}_2\text{Vi}$
- $\text{Me}_2\text{ViSiO}(\text{NaphPhSiO})_m \cdot (\text{MePhSiO})_n \cdot \text{SiMe}_2\text{Vi}$
- $\text{Me}_2\text{ViSiO}(\text{NaphPhSiO})_m \cdot (\text{Ph}_2\text{SiO})_n \cdot \text{SiMe}_2\text{Vi}$
- 5 $\text{MePhViSiO}(\text{NaphPhSiO})_m \cdot \text{SiMePhVi}$
- $\text{MePhViSiO}(\text{NaphPhSiO})_m \cdot (\text{MePhSiO})_n \cdot \text{SiMePhVi}$
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- 10 $\text{Ph}_2\text{ViSiO}(\text{NaphPhSiO})_m \cdot (\text{Ph}_2\text{SiO})_n \cdot \text{SiPh}_2\text{Vi}$
- $\text{Me}_2\text{ViSiO}(\text{AnthMeSiO})_m \cdot \text{SiMe}_2\text{Vi}$
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- $\text{Ph}_2\text{ViSiO}(\text{AnthMeSiO})_m \cdot \text{SiPh}_2\text{Vi}$
- $\text{Ph}_2\text{ViSiO}(\text{AnthMeSiO})_m \cdot (\text{MePhSiO})_n \cdot \text{SiPh}_2\text{Vi}$
- $\text{Ph}_2\text{ViSiO}(\text{AnthMeSiO})_m \cdot (\text{Ph}_2\text{SiO})_n \cdot \text{SiPh}_2\text{Vi}$
- 20 $\text{Me}_2\text{ViSiO}(\text{AnthPhSiO})_m \cdot \text{SiMe}_2\text{Vi}$
- $\text{Me}_2\text{ViSiO}(\text{AnthPhSiO})_m \cdot (\text{MePhSiO})_n \cdot \text{SiMe}_2\text{Vi}$
- $\text{Me}_2\text{ViSiO}(\text{AnthPhSiO})_m \cdot (\text{Ph}_2\text{SiO})_n \cdot \text{SiMe}_2\text{Vi}$
- $\text{MePhViSiO}(\text{AnthPhSiO})_m \cdot \text{SiMePhVi}$



[0029] Component (B) is one of the base compounds of this composition and is an organopolysiloxane resin represented by the average unit formula:



and having at least two alkenyl groups in a molecule.

10 **[0030]** In the formula, R^1 is an alkenyl group having from 2 to 12 carbon atoms, examples of which are the same groups as those described above. In the formula, R^2 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms, examples of which are the same groups as those described above. In the formula, R^4 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, examples of which are the same groups as those described above.

15 **[0031]** In the formula, R^5 is an aryl group having from 6 to 20 carbon atoms or an aralkyl group having from 7 to 20 carbon atoms. Examples of the aryl groups of R^5 include phenyl groups, tolyl groups, xylyl groups, naphthyl groups, anthracenyl groups, phenanthryl groups, pyrenyl groups, and groups in which the hydrogen atoms of these aryl groups are substituted with alkyl groups such as methyl groups and ethyl groups; alkoxy groups such as methoxy groups and ethoxy groups; or halogen atoms such as chlorine atoms and bromine atoms. Of these, phenyl groups and naphthyl groups are preferable. Examples of the aralkyl groups of R^5 include benzyl groups, phenethyl groups, naphthyl ethyl groups, naphthyl propyl groups, anthracenyl ethyl groups, phenanthryl ethyl groups, pyrenyl ethyl groups, and groups in which the hydrogen atoms of these aralkyl groups are substituted with alkyl groups such as methyl groups and ethyl groups; alkoxy groups such as methoxy groups and ethoxy groups; or halogen atoms such as chlorine atoms and bromine atoms.

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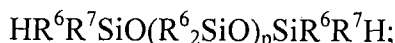
[0032] In the formula, **a**, **b**, and **c** are respectively numbers satisfying $0.01 \leq \mathbf{a} \leq 0.5$, $0 \leq \mathbf{b} \leq 0.7$, $0.1 \leq \mathbf{c} < 0.9$, and $\mathbf{a} + \mathbf{b} + \mathbf{c} = 1$, preferably numbers satisfying $0.05 \leq \mathbf{a} \leq 0.45$, $0 \leq \mathbf{b} \leq 0.5$, $0.4 \leq \mathbf{c} < 0.85$, and $\mathbf{a} + \mathbf{b} + \mathbf{c} = 1$, and even more preferably numbers satisfying $0.05 \leq \mathbf{a} \leq 0.4$, $0 \leq \mathbf{b} \leq 0.4$, $0.45 \leq \mathbf{c} < 0.8$, and $\mathbf{a} + \mathbf{b} + \mathbf{c} = 1$. This is because the gas permeability of the cured product is reduced if **a** is not more than the lower limit of the above-mentioned range and stickiness hardly occurs in the cured product if **a** is not more than the upper limit of the above-mentioned range. This is also because the hardness of the cured product is favorable and the reliability improves when **b** is less than or equal to the upper limit of the range described above. This is also because the refractive index of the cured product is favorable when **c** is greater than or equal to the lower limit of the range described above, and the mechanical characteristics of the cured product improve when **c** is less than or equal to the upper limit of the range described above.

[0033] The organopolysiloxane for component (B) is expressed by the average unit formula described above but may also have siloxane units represented by the formula: $\text{R}^8_3\text{SiO}_{1/2}$, siloxane units represented by the formula: $\text{R}^9\text{SiO}_{3/2}$, or siloxane units represented by the formula: $\text{SiO}_{4/2}$ within a range that does not diminish the object of the present invention. In the formula, R^8 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms. Examples of the alkyl group of R^8 include the same alkyl groups described for R^1 . Examples of the aryl group of R^8 include the same aryl groups described for the aforementioned R^5 . Examples of the aralkyl group of R^8 include the same aralkyl groups described for the aforementioned R^5 . In the formula, R^9 is an alkyl group having from 1 to 12 carbon atoms or an alkenyl group having from 2 to 12 carbon atoms. Examples of the alkyl group of R^9 include the same alkyl groups described for R^5 . Examples of the alkenyl group of R^9 include the same groups described for R^1 . Furthermore, the organopolysiloxane of component (B) may contain silicon-bonded alkoxy groups, such as methoxy groups, ethoxy groups, or propoxy groups, or silicon-bonded hydroxyl groups as long as the objective of the present invention is not impaired.

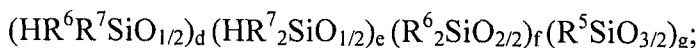
[0034] In this composition, the content of component (B) is in a range of from 10 to 80 mass %, preferably in a range of from 10 to 70 mass %, and more preferably in a range of from 30 to 70 mass % of this composition. This is because when the content of component (B) is greater than or equal to the lower limit of the aforementioned range, it is

possible to impart the cured product with mechanical strength, and when the content is less than or equal to the upper limit of the aforementioned range, it is possible to improve handleability of the resulting composition.

[0035] Component (C) is a crosslinking agent for the present composition, and is an organosiloxane (C₁) represented by general formula:



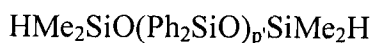
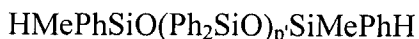
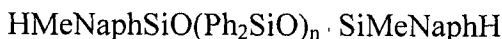
an organopolysiloxane (C₂) represented by the average unit formula:



or a mixture of components (C₁) and (C₂).

[0036] In component (C₁), R⁶ are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms. Examples of the alkyl group of R⁶ include the same alkyl groups described for the aforementioned R², and the alkyl group is preferably a methyl group. Examples of the aryl group of R⁶ include the same aryl groups described for the aforementioned R², and the aryl group is preferably a phenyl group. Examples of the aralkyl group of R⁶ include the same aralkyl groups described for the aforementioned R². In the formulas, R⁷ are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, examples of which include the same alkyl groups as described for the aforementioned R², and are preferably methyl groups. In the formula, **p** is an integer in a range from 0 to 100 and, in order for the composition to exhibit excellent handleability, is preferably an integer in a range from 0 to 30, and more preferably an integer in a range from 0 to 10.

[0037] Examples of this type of component (C₁) include organosiloxanes such as those mentioned below. In the formulas, Me, Ph, and Naph respectively indicate a methyl group, a phenyl group, and a naphthyl group, and **p'** is an integer from 1 to 100.





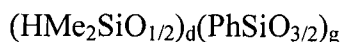
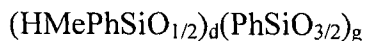
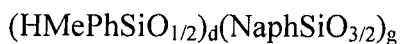
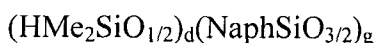
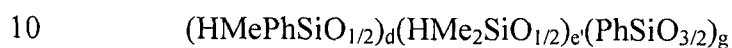
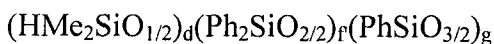
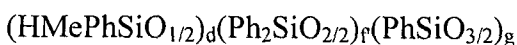
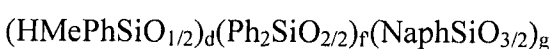
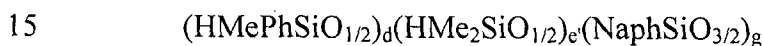
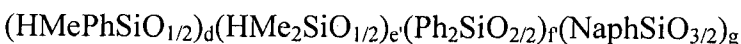
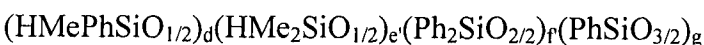
5 [0038] In component (C₂), R⁵ in the formula is an aryl group having from 6 to 20 carbon atoms or an aralkyl group having from 7 to 20 carbon atoms, examples of which are the same groups as those described above. In the formula, R⁶ are the same or different, and are each an alkyl having from 1 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms, examples of which
10 are the same groups as those described above. In the formula, R⁷ are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, examples of which are the same groups as those described above.

[0039] In the formula, **d**, **e**, **f**, and **g** are numbers that satisfy such that $0.1 \leq \mathbf{d} \leq 0.7$, $0 \leq \mathbf{e} \leq 0.5$, $0 \leq \mathbf{f} \leq 0.7$, $0.1 \leq \mathbf{g} < 0.9$, and $\mathbf{d} + \mathbf{e} + \mathbf{f} + \mathbf{g} = 1$, and are preferably numbers that
15 satisfy such that $0.2 \leq \mathbf{d} \leq 0.7$, $0 \leq \mathbf{e} \leq 0.4$, $0 \leq \mathbf{f} < 0.5$, $0.25 \leq \mathbf{g} < 0.7$, and $\mathbf{d} + \mathbf{e} + \mathbf{f} + \mathbf{g} = 1$. This is because the gas permeability of the cured product is reduced if **d** is not less than the lower limit of the above-mentioned range and the cured product has an appropriate hardness if **d** is not more than the upper limit of the above-mentioned range. In addition, the refractive index of the cured product is improved if **e** is not more than the upper limit of
20 the above-mentioned range. In addition, the cured product has an appropriate hardness and the reliability of an optical semiconductor device prepared using the present composition is improved if **f** is not more than the upper limit of the above-mentioned range. In addition, the refractive index of the cured product is increased if **g** is not less than the lower limit of the above-mentioned range and the mechanical strength of the cured product
25 is improved if **g** is not more than the upper limit of the above-mentioned range.

[0040] The molecular weight of this type of component (C₂) is not particularly limited, but from the perspectives of the handleability of the composition and the mechanical strength of the cured product, the mass average molecular weight in terms of standard polystyrene, as measured by gel permeation chromatography, is preferably from 500 to
30 10,000, and more preferably from 500 to 2,000.

[0041] Examples of this type of component (C₂) include organopolysiloxanes such as those mentioned below. Moreover, Me, Ph, and Naph in the formulae below denote a methyl group, a phenyl group, and a naphthyl group respectively, and **d**, **e'**, **f'**, and **g** are numbers that satisfy such that $0.1 \leq \mathbf{d} \leq 0.7$, $0 < \mathbf{e}' \leq 0.5$, $0 < \mathbf{f}' \leq 0.7$, $0.1 \leq \mathbf{g} < 0.9$, and

5. $\mathbf{d} + \mathbf{e}' + \mathbf{f}' + \mathbf{g} = 1$.



[0042] Component (C) can be component (C₁), component (C₂), or a mixture of components (C₁) and (C₂). In cases where a mixture of components (C₁) and (C₂) is used, the mixing ratio is not particularly limited, but it is preferable for the ratio of mass of component (C₁) : mass of component (C₂) to be from 0.5:9.5 to 9.5:0.5.

[0043] The content of component (C) in the present composition, per 1 mol of total alkenyl groups in components (A) and (B), is in a range such that the silicon-bonded hydrogen atoms in component (C) is in a range of 0.1 to 5 mol, and preferably in a range of 0.5 to 2 mol. This is because when the content of component (C) is greater than or equal to the lower limit of the range described above, the composition is cured sufficiently, and when the content is less than or equal to the upper limit of the range described above, the heat resistance of the cured product improves, thus making it possible to improve the reliability of an optical semiconductor device produced using this composition.

[0044] Component (D) is a hydrosilylation reaction catalyst for accelerating the curing of this composition, and examples include platinum-based catalysts, rhodium-based catalysts, and palladium-based catalysts. Particularly, component (D) is preferably a platinum-based catalyst so that the curing of the present composition can be dramatically accelerated. Examples of the platinum-based catalyst include a platinum fine powder, chloroplatinic acid, an alcohol solution of chloroplatinic acid, a platinum-alkenylsiloxane complex, a platinum-olefin complex and a platinum-carbonyl complex, with a platinum-alkenylsiloxane complex being preferred.

[0045] The content of component (D) in this composition is an effective amount for accelerating the curing of the composition. Specifically, in order to be able to sufficiently accelerate the curing reaction of this composition, the content of component (D) is preferably an amount so that the catalyst metal in component (D) is in the range of 0.01 to 500 ppm, more preferably in the range of 0.01 to 100 ppm, and particularly preferably in the range of 0.01 to 50 ppm in mass units with respect to this composition.

[0046] This composition may also contain an adhesion-imparting agent in order to improve the adhesiveness of the cured product with respect to the substrate with which the composition makes contact during the course of curing. Preferred adhesion-imparting agents are organosilicon compounds having at least one alkoxy group bonded to a silicon atom in a molecule. This alkoxy group is exemplified by a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and a methoxyethoxy group; and the methoxy group is particularly preferred. Moreover, non-alkoxy groups bonded to a silicon atom of this organosilicon compound are exemplified by substituted or non-substituted monovalent hydrocarbon groups such as alkyl groups, alkenyl groups, aryl groups, aralkyl groups, halogenated alkyl groups and the like; epoxy group-containing monovalent organic groups such as glycidoxyalkyl groups (such as a 3-glycidoxypropyl group, a 4-glycidoxybutyl group, and the like), epoxycyclohexylalkyl groups (such as a 2-(3,4-epoxycyclohexyl)ethyl group, a 3-(3,4-epoxycyclohexyl)propyl group, and the like) and oxiranylalkyl groups (such as a 4-oxiranylbutyl group, an 8-oxiranyloctyl group, and the like); acrylic group-containing monovalent organic groups such as a 3-methacryloxypropyl group and the like; and a hydrogen atom. This organosilicon compound preferably has a silicon-bonded alkenyl group or silicon-bonded hydrogen atom. Moreover, due to the ability to impart good adhesion with respect to various types of substrates, this organosilicon compound preferably has at least one epoxy group-containing monovalent organic group in a

molecule. This type of organosilicon compound is exemplified by organosilane compounds, organosiloxane oligomers and alkyl silicates. Molecular structure of the organosiloxane oligomer or alkyl silicate is exemplified by a linear structure, partially branched linear structure, branched chain structure, ring-shaped structure, and net-shaped structure. A linear chain structure, branched chain structure, and net-shaped structure are particularly preferred. This type of organosilicon compound is exemplified by silane compounds such as 3-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-methacryloxy propyltrimethoxysilane, and the like; siloxane compounds having at least one of silicon-bonded alkenyl groups and silicon-bonded hydrogen atoms, and at least one silicon-bonded alkoxy group in a molecule; mixtures of a silane compound or siloxane compound having at least one silicon-bonded alkoxy group and a siloxane compound having at least one silicon-bonded hydroxyl group and at least one silicon-bonded alkenyl group in a molecule; and methyl polysilicate, ethyl polysilicate, and epoxy group-containing ethyl polysilicate. The content of the adhesion-imparting agent in the present composition is not particularly limited but is preferably in the range of 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of the components (A) to (D) described above so as to ensure favorable adhesion to the substrate with which the composition makes contact during the course of curing.

[0047] In addition to component (A) described above, this composition may also contain a straight-chain organopolysiloxane having at least two alkenyl groups and not having silicon-bonded hydrogen atoms in a molecule in order to impart the cured product with softness, extensibility, and flexibility. Examples of the alkenyl group in this organopolysiloxane include alkenyl groups having from 2 to 12 carbon atoms such as vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, heptenyl groups, octenyl groups, nonenyl groups, decenyl groups, undecenyl groups, and dodecenyl groups, and vinyl groups are preferable. Examples of groups bonding to silicon atoms other than alkenyl groups include alkyl groups having from 1 to 12 carbon atoms such as methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, and dodecyl groups; aryl groups having from 6 to 20 carbon atoms such as phenyl groups, tolyl groups, xylyl groups, naphthyl groups, anthracenyl groups, phenanthryl groups, pyrenyl groups, and groups in which the hydrogen atoms of these aryl groups are substituted with alkyl groups such as methyl groups or ethyl groups; alkoxy groups such as methoxy groups or ethoxy

groups, or halogen atoms such as chlorine atoms or bromine atoms; aralkyl groups having from 7 to 20 carbon atoms such as benzyl groups, phenethyl groups, naphthylethyl groups, naphthylpropyl groups, anthracenylethyl groups, phenanthrylethyl groups, pyrenylethyl groups, and groups in which the hydrogen atoms of these aralkyl groups are substituted with alkyl groups such as methyl groups or ethyl groups; alkoxy groups such as methoxy groups or ethoxy groups, or halogen atoms such as chlorine atoms or bromine atoms; or halogenated alkyl groups having from 1 to 12 carbon atoms such as chloromethyl groups or 3,3,3-trifluoropropyl groups.

[0048] Examples of such an organopolysiloxane include copolymers of

dimethylsiloxanes and methylvinylsiloxanes capped at both molecular terminals with trimethylsiloxy groups, methylvinylpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, copolymers of dimethylsiloxanes, methylvinylsiloxanes, and methylphenylsiloxanes capped at both molecular terminals with trimethylsiloxy groups, dimethylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, methylvinylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, methylphenylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, copolymers of dimethylsiloxanes and methylvinylsiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, copolymers of dimethylsiloxanes, methylvinylsiloxanes, and methylphenylsiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, methylphenylpolysiloxanes capped at both molecular terminals with methylphenylvinylsiloxy groups, methylphenylpolysiloxanes capped at both molecular terminals with diphenylvinylsiloxy groups, copolymers of methylphenylsiloxane and diphenylsiloxanes capped at both molecular terminals with methylphenylvinylsiloxy groups, copolymers of methylphenylsiloxane and diphenylsiloxanes capped at both molecular terminals with diphenylvinylsiloxy groups, and mixtures of two or more types of these organopolysiloxanes.

[0049] A reaction inhibitor, for example, an alkyne alcohol such as 2-methyl-3-butyne-2-ol, 3,5-dimethyl-1-hexyne-3-ol and 2-phenyl-3-butyne-2-ol; an ene-yne compound such as 3-methyl-3-penten-1-yne and 3,5-dimethyl-3-hexen-1-yne; or 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane or a benzotriazole may be incorporated as an optional component in the present composition. The content of the reaction inhibitor in this composition is not particularly limited but is

preferably in the range of 0.0001 to 5 parts by mass with respect to a total of 100 parts by mass of components (A) to (D) described above.

[0050] This composition may also contain a fluorescent substance as an optional component. This fluorescent substance is exemplified by substances widely used in light emitting diodes (LEDs), such as yellow, red, green, and blue light-emitting fluorescent substances such as oxide fluorescent substances, oxynitride fluorescent substances, nitride fluorescent substances, sulfide fluorescent substances, oxysulfide fluorescent substances, and the like. Examples of oxide fluorescent substances include yttrium, aluminum, and garnet-type YAG green to yellow light-emitting fluorescent substances containing cerium ions; terbium, aluminum, and garnet-type TAG yellow light-emitting fluorescent substances containing cerium ions; and silicate green to yellow light-emitting fluorescent substances containing cerium or europium ions. Examples of oxynitride fluorescent substances include silicon, aluminum, oxygen, and nitrogen-type SiAlON red to green light-emitting fluorescent substances containing europium ions. Examples of nitride fluorescent substances include calcium, strontium, aluminum, silicon, and nitrogen-type cousin red light-emitting fluorescent substances containing europium ions. Examples of sulfide fluorescent substances include ZnS green light-emitting fluorescent substances containing copper ions or aluminum ions. Examples of oxysulfide fluorescent substances include Y_2O_2S red light-emitting fluorescent substances containing europium ions. These fluorescent substances may be used as one type or as a mixture of two or more types. The content of the fluorescent substance in this composition is not particularly limited but is preferably in the range of 0.1 to 70 mass% and more preferably in the range of 1 to 20 mass% in this composition.

[0051] Moreover, an inorganic filler such as silica, glass, alumina or zinc oxide; an organic resin fine powder of a polymethacrylate resin and the like; a heat-resistant agent, a dye, a pigment, a flame retardant, a solvent and the like may be incorporated as optional components in the present composition at levels that do not impair the objective of the present invention.

[0052] Of the components added as optional components, in order to sufficiently suppress the discoloration of the silver electrodes or the silver plating of the substrate in the optical semiconductor device due to sulfur-containing gas in the air, it is possible to add at least one type of a fine powder having an average particle size from 0.1 nm to 5 μ m selected from a group comprising zinc oxide fine powders surface-coated with at least one

type of oxide of an element selected from a group comprising Al, Ag, Cu, Fe, Sb, Si, Sn, Ti, Zr, and rare earth elements, zinc oxide fine powders surface-treated with organic silicon compounds not having alkenyl groups, and hydrate fine powders of zinc carbonate.

[0053] In a zinc oxide fine powder surface-coated with an oxide, examples of rare earth elements include yttrium, cerium, and europium. Examples of oxides on the surface of the zinc oxide powder include Al_2O_3 , AgO , Ag_2O , Ag_2O_3 , CuO , Cu_2O , FeO , Fe_2O_3 , Fe_3O_4 , Sb_2O_3 , SiO_2 , SnO_2 , Ti_2O_3 , TiO_2 , Ti_3O_5 , ZrO_2 , Y_2O_3 , CeO_2 , Eu_2O_3 , and mixtures of two or more types of these oxides.

[0054] In a zinc oxide powder surface-treated with an organosilicon compound, the organosilicon compound does not have alkenyl groups, and examples include organosilanes, organosilazanes, polymethylsiloxanes, organohydrogenpolysiloxanes, and organosiloxane oligomers. Specific examples include organochlorosilanes such as trimethylchlorosilane, dimethylchlorosilane, and methyltrichlorosilane; organotrialkoxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, phenyltrimethoxysilane, ethyltrimethoxysilane, n-propyltrimethoxysilane, and γ -methacryloxypropyltrimethoxysilane; diorganodialkoxysilanes such as dimethyldimethoxysilane, dimethyldiethoxysilane, and diphenyldimethoxysilane; triorganoalkoxysilanes such as trimethylmethoxysilane and trimethylethoxysilane; partial condensates of these organoalkoxysilanes; organosilazanes such as hexamethyldisilazane; polymethylsiloxanes, organohydrogenpolysiloxanes, organosiloxane oligomers having a silanol group or an alkoxy group, and resin-like organopolysiloxanes consisting of an $\text{R}^8\text{SiO}_{3/2}$ unit (wherein R^8 is a monovalent hydrocarbon group excluding alkenyl groups, examples of which include alkyl groups such as methyl groups, ethyl groups, or propyl groups; and aryl groups such as phenyl groups) or an $\text{SiO}_{4/2}$ unit, and having a silanol group or an alkoxy group.

[0055] A hydrate fine powder of zinc carbonate is a compound in which water bonds to zinc carbonate, and a preferable compound is one in which the rate of weight decrease is at least 0.1 wt. % under heating conditions at 105°C for 3 hours.

[0056] The content of the zinc oxide is an amount in a range from 1 ppm to 10% and preferably an amount in a range from 1 ppm to 5% of the composition in terms of mass units. This is because when the content of the component is greater than or equal to the lower limit of the range described above, the discoloration of the silver electrodes or the silver plating of the substrate in the optical semiconductor device due to a sulfur-

containing gas is sufficiently suppressed, and when the content is less than or equal to the upper limit of the range described above, the fluidity of the resulting composition is not diminished.

[0057] In addition, the composition may also contain a triazole-based compound as an optional component to enable the further suppression of the discoloration of the silver electrodes or the silver plating of the substrate due to a sulfur-containing gas in the air. Examples of such components include 1H-1,2,3-triazole, 2H-1,2,3-triazole, 1H-1,2,4-triazole, 4H-1,2,4-triazole, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 1H-1,2,3-triazole, 2H-1,2,3-triazole, 1H-1,2,4-triazole, 4H-1,2,4-triazole, benzotriazole, tolyltriazole, carboxybenzotriazole, 1H-benzotriazole-5-methylcarboxylate, 3-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 5-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, chlorobenzotriazole, nitrobenzotriazole, aminobenzotriazole, cyclohexano[1,2-d]triazole, 4,5,6,7-tetrahydroxytolyltriazole, 1-hydroxybenzotriazole, ethylbenzotriazole, naphthotriazole, 1-N,N-bis(2-ethylhexyl)-[(1,2,4-triazole-1-yl)methyl]amine, 1-[N,N-bis(2-ethylhexyl)aminomethyl]benzotriazole, 1-[N,N-bis(2-ethylhexyl)aminomethyl]tolyltriazole, 1-[N,N-bis(2-ethylhexyl)aminomethyl]carboxybenzotriazole, 1-[N,N-bis(2-hydroxyethyl)-aminomethyl]benzotriazole, 1-[N,N-bis(2-hydroxyethyl)-aminomethyl]tolyltriazole, 1-[N,N-bis(2-hydroxyethyl)-aminomethyl]carboxybenzotriazole, 1-[N,N-bis(2-hydroxypropyl)aminomethyl]carboxybenzotriazole, 1-[N,N-bis(1-butyl)aminomethyl]carboxybenzotriazole, 1-[N,N-bis(1-octyl)aminomethyl]carboxybenzotriazole, 1-(2',3'-di-hydroxypropyl)benzotriazole, 1-(2',3'-di-carboxyethyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-aminophenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole, 1-hydroxybenzotriazole-6-carboxylic acid, 1-oleoylbenzotriazole, 1,2,4-triazol-3-ol, 5-amino-3-mercapto-1,2,4-triazole, 5-amino-1,2,4-triazole-3-carboxylic acid, 1,2,4-triazole-3-carboxamide, 4-aminourazole, and 1,2,4-triazol-5-one. The content of this benzotriazole compound is not particularly limited but is an amount in a range from 0.01 ppm to 3% and preferably in a range from 0.1 ppm to 1% of the composition in terms of mass units.

[0058] The present composition is such that curing occurs either at room temperature or under heating, but it is preferable to heat the composition in order to achieve rapid curing. The heating temperature is preferably from 50 to 200°C.

[0059] The cured product of the present invention will now be described in detail.

[0060] The cured product of the present invention is formed by curing the aforementioned curable silicone composition. The shape of the cured product is not particularly limited, and examples include a sheet shape and a film shape. The cured product can be handled as a simple substance or may also be handled in a state in which the cured product covers or seals an optical semiconductor element or the like.

[0061] The optical semiconductor device of the present invention will now be explained in detail.

[0062] The optical semiconductor device of the present invention is produced by sealing an optical semiconductor element with a cured product of the curable silicone composition described above. Examples of such an optical semiconductor device of the present invention include a light emitting diode (LED), a photocoupler, and a CCD. Examples of optical semiconductor elements include light emitting diode (LED) chips and solid-state image sensing devices.

[0063] Figure 1 illustrates a cross-sectional view of a single surface mounted type LED, which is one example of the optical semiconductor device of the present invention. In the LED illustrated in Figure 1, an LED chip 1 is die-bonded to a lead frame 2, and the LED chip 1 and a lead frame 3 are wire-bonded by a bonding wire 4. A casing material 5 is provided around this LED chip 1, and the LED chip 1 inside the casing material 5 is sealed by a cured product 6 of the curable silicone composition of the present invention.

[0064] An example of a method of producing the surface mounted type LED illustrated in Figure 1 is a method of die-bonding the LED chip 1 to the lead frame 2, wire-bonding the LED chip 1 and the lead frame 3 with a gold bonding wire 4, filling the inside of the casing material 5 provided around the LED chip 1 with the curable silicone composition of the present invention, and then curing the composition by heating at 50 to 200°C.

Examples

[0065] The curable silicone composition, the cured product thereof, and the optical semiconductor device of the present invention will be described in detail hereinafter using Practical and Comparative Examples. The viscosity is the value at 25°C, and in Practical and Comparative Examples, the viscosity is the value at 25°C, and Me, Vi, Ph, and Naph respectively represent a methyl group, a vinyl group, a phenyl group, and a naphthyl group.

The characteristics of the cured product of the curable silicone composition were measured as follows.

[0066]

[Refractive index of the cured product]

- 5 A cured product is produced by heating the curable silicone composition at 150°C for 2 hours in a circulating hot air oven. The refractive index of this cured product at 25°C and a wavelength of 633 nm was measured using a refractometer.

[0067]

[Water vapor permeability of the cured product]

- 10 A cured film with a thickness of 1 mm was prepared by curing the curable silicone composition for 2 hours at 150°C using a press. The water vapor permeability of the cured film was measured in accordance with the cup method of JIS Z0208 under conditions with a temperature of 40°C and 90% relative humidity.

[0068]

- 15 [Reference Example 1]

72.3 g (0.388 mol) of 1,3-divinyltetramethyldisiloxane, 31.1 g (0.517 mol) of acetic acid, and 0.17 g (1.14 mmol) of trifluoromethanesulfonic acid were placed in a reaction vessel, and 60.0 g (0.259 mol) of naphthylmethyldimethoxysilane was added dropwise into the mixture while heating to 45 to 50°C. After completion of drop-wise addition, the mixture was heated and stirred for 30 minutes at 50°C. While the system was maintained at a temperature of 60°C or less, 26.4 g (0.259 mol) of acetic anhydride was added dropwise to the mixture. After completion of dropwise addition, the mixture was heated and stirred for 30 minutes at 50°C. Next, toluene and water were added, and after the mixture was stirred, the mixture was left to stand. The water layer of the lower layer was extracted, and the toluene layer of the upper layer was repeatedly washed with water. The water layer of the lower layer was then extracted, and low-boiling-point substances were distilled out of the toluene layer while heating under reduced pressure, thereby producing 84.4 g (yield: 87.7%) of a clear, liquid organopolysiloxane represented by the formula:

- 30 $\text{Me}_2\text{ViSiOMeNaphSiOSiMe}_2\text{Vi}$

(refractive index: 1.514, viscosity: 9.6 mPa·s).

[0069]

[Reference Example 2]

58.8 g (0.190 mol) of 1,3-divinyl-1,3-diphenyldimethyldisiloxane, 20.7 g (0.345 mol) of acetic acid, and 0.27 g (1.83 mmol) of trifluoromethanesulfonic acid were added to a reaction vessel, and 40.0 g (0.172 mol) of naphthylmethyldimethoxysilane was added dropwise into the mixture while heating to 45 to 50°C. After completion of drop-wise addition, the mixture was heated and stirred for 30 minutes at 50°C. While the system was maintained at a temperature of 60°C or less, 17.6 g (0.172 mol) of acetic anhydride was added dropwise to the mixture. After completion of dropwise addition, the mixture was heated and stirred for 30 minutes at 50°C. Next, toluene and water were added, and after the mixture was stirred, the mixture was left to stand. The water layer of the lower layer was extracted, and the toluene layer of the upper layer was repeatedly washed with water. The water layer of the lower layer was then extracted, and low-boiling-point substances were distilled out of the toluene layer while heating under reduced pressure, thereby producing 83.7 g (yield: 97.8%) of a clear, liquid organopolysiloxane represented by the formula:



(refractive index: 1.559, viscosity: 25.1 mPa·s).

[0070]

[Reference Example 3]

14.3 g (0.077 mol) of 1,3-divinyldimethyltetramethyldisiloxane, 6.1 g (0.102 mol) of acetic acid, and 0.04 g (0.24 mmol) of trifluoromethanesulfonic acid were placed in a reaction vessel, and 15.0 g (0.051 mol) of naphthylphenyldimethoxysilane was added dropwise into the mixture while heating to 45 to 50°C. After completion of drop-wise addition, the mixture was heated and stirred for 30 minutes at 50°C. While the system was maintained at a temperature of 60°C or less, 5.21 g (0.051 mol) of acetic anhydride was added dropwise to the mixture. After completion of dropwise addition, the mixture was heated and stirred for 30 minutes at 50°C. Next, toluene and water were added, and after the mixture was stirred, the mixture was left to stand. The water layer of the lower layer was extracted, and the toluene layer of the upper layer was repeatedly washed with water. The water layer of the lower layer was then extracted, and low-boiling-point substances were distilled out of the toluene layer while heating under reduced pressure, thereby producing 21.6 g (yield: 97.5%) of a clear, liquid organopolysiloxane represented by the formula:

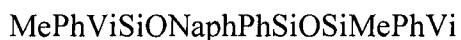


(refractive index: 1.548, viscosity: 64.3 mPa·s).

[0071]

[Reference Example 4]

- 5 29.0 g (0.094 mol) of 1,3-divinyl-1,3-diphenyldimethyldisiloxane, 10.2 g (0.170 mol) of acetic acid, and 0.15 g (0.97 mmol) of trifluoromethanesulfonic acid were added to a reaction vessel, and a mixture of 25.0 g (0.085 mol) of naphthylphenyldimethoxysilane and 25.0 g of toluene was added dropwise into the mixture while heating to 45 to 50°C. After completion of drop-wise addition, the mixture was heated and stirred for 30 minutes
- 10 at 50°C. While the system was maintained at a temperature of 60°C or less, 8.68 g (0.085 mol) of acetic anhydride was added dropwise to the mixture. After completion of dropwise addition, the mixture was heated and stirred for 30 minutes at 50°C. Next, toluene and water were added and repeatedly stirred, left to stand, and relieved of the lower layer. After the mixture was washed with water, the low-boiling-point substances were
- 15 distilled out of the toluene layer serving as the upper layer, thereby producing 45.4 g (yield: 95.7%) of a clear, liquid organopolysiloxane represented by the formula:



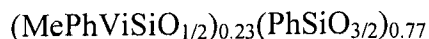
(refractive index: 1.582, viscosity: 6168.4 mPa·s).

[0072]

- 20 [Reference Example 5]

- First, 400 g (2.02 mol) of phenyltrimethoxysilane and 93.5 g (0.30 mol) of 1,3-divinyl-1,3-diphenyldimethyldisiloxane were loaded into a reaction vessel and mixed in advance. Next, 1.74 g (11.6 mmol) of trifluoromethane sulfonic acid was added, and 110 g (6.1 mol) of water was added and heat-refluxed for 2 hours while stirring. The mixture
- 25 was then distilled at atmospheric pressure by heating until the mixture reached 85°C. Next, 89 g of toluene and 1.18 g (21.1 mmol) of potassium hydroxide were added, and after the mixture was distilled at atmospheric pressure by heating until the reaction temperature reached 120°C, the mixture was reacted for 6 hours at this temperature. The mixture was cooled to room temperature, and a neutralization reaction was performed by
- 30 adding 0.68 g (11.4 mmol) of acetic acid. The produced salt was filtered, and low boiling point substances were removed from the obtained transparent solution by heating under

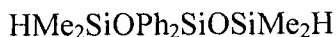
reduced pressure, thereby producing 347 g (yield: 98%) of an organopolysiloxane resin represented by the average unit formula:



[0073]

5 [Practical Example 1]

10.0 parts by mass of the organopolysiloxane prepared in Reference Example 3,
62.8 parts by mass of the organopolysiloxane resin prepared in Reference Example 5,
27.2 parts by mass of an organotrisiloxane represented by the formula:

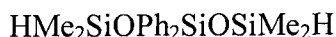


10 (an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed,
15 thereby producing a curable silicone composition having a viscosity of 952 mPa·s. The refractive index of a cured product of this curable silicone composition was 1.565, and the water vapor transmission rate was 6.5 g/m²·24h.

[0074]

[Practical Example 2]

20 20.4 parts by mass of the organopolysiloxane prepared in Reference Example 3,
48.5 parts by mass of the organopolysiloxane resin prepared in Reference Example 5,
31.1 parts by mass of an organotrisiloxane represented by the formula:

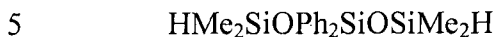


(an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed,
25 thereby producing a curable silicone composition having a viscosity of 218.7 mPa·s. The refractive index of a cured product of this curable silicone composition was 1.563, and the water vapor transmission rate was 7.2 g/m²·24h.
30

[0075]

[Practical Example 3]

10.0 parts by mass of the organopolysiloxane prepared in Reference Example 4,
64.1 parts by mass of the organopolysiloxane resin prepared in Reference Example 5,
25.9 parts by mass of an organotrisiloxane represented by the formula:



(an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-

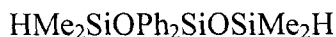
10 tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed, thereby producing a curable silicone composition having a viscosity of 1359.9 mPa·s.

The refractive index of a cured product of this curable silicone composition was 1.569 , and the water vapor transmission rate was 6.5 g/m²·24h.

[0076]

15 [Practical Example 4]

20.6 parts by mass of the organopolysiloxane prepared in Reference Example 4,
51.0 parts by mass of the organopolysiloxane resin prepared in Reference Example 5,
28.4 parts by mass of an organotrisiloxane represented by the formula:



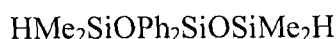
20 (an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-

25 tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed, thereby producing a curable silicone composition. The water vapor transmission rate of a cured product of this curable silicone composition was 7.3 g/m²·24h.

[0077]

[Practical Example 5]

20.2 parts by mass of the organopolysiloxane prepared in Reference Example 1,
30 46.7 parts by mass of the organopolysiloxane resin prepared in Reference Example 5,
33.1 parts by mass of an organotrisiloxane represented by the formula:

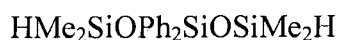


(an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed, thereby producing a curable silicone composition having a viscosity of 109.8 mPa·s. The water vapor transmission rate of a cured product of this curable silicone composition was 9.9 g/m²·24h.

[0078]

10 [Practical Example 6]

10.3 parts by mass of the organopolysiloxane prepared in Reference Example 2, 62.8 parts by mass of the organopolysiloxane resin prepared in Reference Example 5, 26.9 parts by mass of an organotrisiloxane represented by the formula:

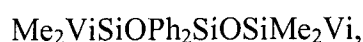


15 (an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed, thereby producing a curable silicone composition having a viscosity of 777.7 mPa·s. The refractive index of a cured product of this curable silicone composition was 1.566, and the water vapor transmission rate was 6.8 g/m²·24h.

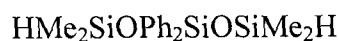
[0079]

[Comparative Example 1]

25 10.2 parts by mass of an organopolysiloxane represented by the formula:



61.8 parts by mass of the organopolysiloxane resin prepared in Reference Example 5, 28.1 parts by mass of an organotrisiloxane represented by the formula:



30 (an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-

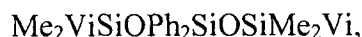
1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed, thereby producing a curable silicone composition having a viscosity of 613.4 mPa·s. The water vapor transmission rate of a cured product of this curable silicone composition was

5 8.0 g/m²·24h.

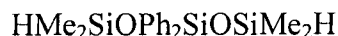
[0080]

[Comparative Example 2]

20.5 parts by mass of an organopolysiloxane represented by the formula:



10 46.7 parts by mass of the organopolysiloxane resin prepared in Reference Example 5, 32.8 parts by mass of an organotrisiloxane represented by the formula:



(an amount at which the quantity of silicon-bonded hydrogen atoms in the component is 1 mole with respect to a total of 1 mole of the vinyl groups in the organopolysiloxane and the organopolysiloxane resin), and 0.25 parts by mass of a solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (the solution containing 0.1 mass % of platinum) were mixed, thereby producing a curable silicone composition having a viscosity of 99.3 mPa·s. The water vapor transmission rate of a cured product of this curable silicone composition was

15 11.0 g/m²·24h.

20

Industrial Applicability

[0081] The curable silicone composition of the present invention has excellent handleability and can form a curable product which undergoes minimal yellowing due to thermal aging and sufficiently suppresses the discoloration of silver electrodes or the silver plating of a substrate due to a sulfur-containing gas in the air. Therefore, the curable silicone composition is suitable as a sealant, a coating agent, or an adhesive for an optical semiconductor element of an optical semiconductor device or a protective agent for the silver electrodes or the silver plating of a substrate of a liquid crystal terminal part.

25

Description of Symbols

30 [0082]

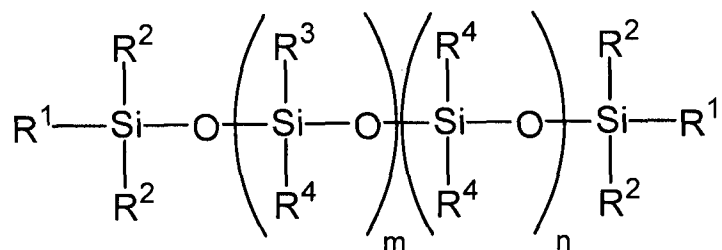
1 Optical semiconductor element

- 2 Lead frame
- 3 Lead frame
- 4 Bonding wire
- 5 Casing material
- 5 6 Cured product of the curable silicone composition

CLAIMS

1. A curable silicone composition comprising:

(A) an organopolysiloxane represented by the general formula:



5 wherein R^1 are the same or different, and are each an alkenyl group having from 2 to 12 carbons; R^2 are the same or different, and are each an alkyl group having from 1 to 12 carbons, an alkenyl group having from 2 to 12 carbon atoms, an aryl group having from 6 to 20 carbons, or an aralkyl group having from 7 to 20 carbons; R^3 is a condensed polycyclic aromatic group or a group containing a
10 condensed polycyclic aromatic group; R^4 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; and m is an integer from 1 to 100, n is an integer from 0 to 100, where $1 \leq m + n \leq 100$;

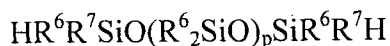
(B) an organopolysiloxane resin represented by the average unit formula:



wherein R^1 , R^2 , and R^4 are synonymous with those described above, R^5 is an aryl group having from 6 to 20 carbon atoms or an aralkyl group having from 7 to 20 carbon atoms; and a , b , and c are respectively numbers satisfying $0.01 \leq a \leq 0.5$, $0 \leq b \leq 0.7$, $0.1 \leq c < 0.9$, and $a + b + c = 1$,

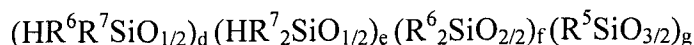
20 and having at least two alkenyl groups in a molecule, in an amount of 10 to 80 mass% of the composition;

(C) an organosiloxane (C_1) represented by the general formula:



25 wherein R^6 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms, an aryl group having from 6 to 20 carbon atoms, or an aralkyl group having from 7 to 20 carbon atoms; R^7 are the same or different, and are each an alkyl group having from 1 to 12 carbon atoms; and p is an integer from 0 to 100;

an organopolysiloxane (C₂) having at least two silicon-bonded hydrogen atoms in a molecule and represented by the average unit formula:



wherein R⁵, R⁶, and R⁷ are synonymous with those described above; and **d**, **e**, **f**,

5 and **g** are numbers that satisfy such that $0.01 \leq \mathbf{d} \leq 0.7$, $0 \leq \mathbf{e} \leq 0.5$, $0 \leq \mathbf{f} \leq 0.7$,

$0.1 \leq \mathbf{g} < 0.9$, and $\mathbf{d} + \mathbf{e} + \mathbf{f} + \mathbf{g} = 1$; or

a mixture of components (C₁) and (C₂), in an amount such that the number of silicon-bonded hydrogen atoms in the present component is from 0.1 to 5 moles per 1 mol of total alkenyl groups in components (A) and (B); and

10 (D) an effective amount of a hydrosilylation reaction catalyst.

2. The curable silicone composition according to claim 1, wherein R³ in component (A) is a naphthyl group.

3. The curable silicone composition according to claim 1 or 2, wherein R⁵ in component (B) is a phenyl group or a naphthyl group.

15 4. A cured product produced by curing the curable silicone composition described in any one of claims 1 to 3.

5. An optical semiconductor device comprising an optical semiconductor element sealed by means of a cured product of the curable silicone composition described in any one of claims 1 to 3.

20

Figure 1

