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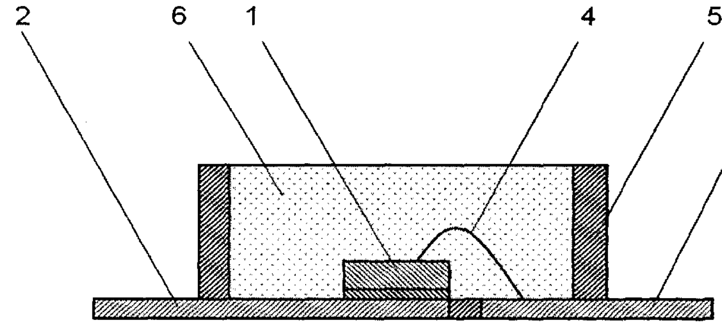
(54) Title: CURABLE SILICONE COMPOSITION, CURED PRODUCT THEREOF, AND OPTICAL SEMICONDUCTOR DEVICE

Figure 1



(57) Abstract: The present invention relates to a curable silicone composition comprising: (A) an organopolysiloxane represented by a specific average unit formula and having at least two alkenyl groups in a molecule, (B) an optional straight-chain organopolysiloxane having at least two alkenyl groups and not having any silicon-bonded hydrogen atoms in a molecule, (C) an organopolysiloxane having at least two silicon-bonded hydrogen atoms in a molecule, wherein at least 80 mass% of this component comprises an organotrisiloxane represented by the formula: $H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H$, and (D) a hydrosilylation reaction catalyst. The curable silicone composition has excellent handleability and high reactivity and forms a cured product with low gas permeability.

DESCRIPTION

CURABLE SILICONE COMPOSITION, CURED PRODUCT THEREOF, AND OPTICAL SEMICONDUCTOR DEVICE

Technical Field

[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. 2012-235184, filed on October 24, 2012, the content of which is incorporated herein by reference.

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, since the gas permeability of a cured product of a curable silicone composition is high, problems such as the discoloration of the sealing material due to corrosive gas and the reduction of brightness due to the corrosion of silver plate on the LED substrate occur when used in a high-brightness LED with high optical intensity and a large amount of heat generation.

[0004] Therefore, a curable silicone composition comprising a branched-chain organopolysiloxane having methylphenylvinylsiloxane units, an organohydrogenpolysiloxane, and an addition reaction catalyst is proposed in Japanese Unexamined Patent Application Publication No. 2012-052045 as a curable silicone composition which forms a cured product with low gas permeability.

[0005] However, such a curable silicone composition has high viscosity, poor handleability, and a slow curing reaction rate, which leads to the problem that a large amount of time and energy is required to complete the curing reaction.

[0006] An object of the present invention is to provide a curable silicone composition having excellent handleability and high reactivity and forming a cured product with low gas permeability. Another object of the present invention is to provide a cured product with low gas permeability and further to provide an optical semiconductor device with excellent reliability.

Disclosure of Invention

[0007] The curable silicone composition of the present invention comprises:

(A) an organopolysiloxane having at least two alkenyl groups in a molecule and represented by the following average unit formula:

$$(R^1R^2R^3SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c$$

wherein, R^1 is an alkyl group having from 1 to 12 carbons; R^2 are the same or different aryl groups having from 6 to 20 carbons or aralkyl groups having from 7 to 20 carbons; R^3 is an alkenyl group having from 2 to 12 carbons; R^4 are the same or different alkyl groups having from 1 to 12 carbons, alkenyl groups having from 2 to 12 carbons, or phenyl groups; 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 $a+b+c=1$;

(B) a straight-chain organopolysiloxane having at least two alkenyl groups and not having any silicon-bonded hydrogen atoms in a molecule, in 0 to 70 mass% of this composition;

(C) an organopolysiloxane having at least two silicon-bonded hydrogen atoms in a molecule, and at least 80 mass% of this component comprising an organotrisiloxane represented by the following formula:

$$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H,$$

in an amount that the amount of silicon-bonded hydrogen atoms in this component is from 0.1 to 5 mol per 1 mol of total alkenyl groups in components (A) and (B); and

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

[0008] The cured product of the present invention is formed by curing the aforementioned curable silicone composition.

[0009] 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

[0010] The curable silicone composition of the present invention is characterized by having excellent handleability and high reactivity and forming a cured product with low gas permeability. In addition, the cured product of the present invention is characterized in that the gas permeability is low. The optical semiconductor device of the present invention is characterized by having excellent reliability.

Brief Description of the Drawings

[0011] Figure 1 is a cross-sectional view of an LED that is an example of the optical semiconductor device of the present invention.

Detailed Description of the Invention

[0012] First, the curable silicone composition of the present invention will be described in detail.

[0013] The organopolysiloxane for component (A), which is the main component of this composition, is represented by the following average unit formula:

$$(R^1R^2R^3SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c$$

and has at least two alkenyl groups in a molecule.

[0014] In the formula, R^1 is an alkyl group having from 1 to 12 carbons, examples of which 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, of these, methyl groups are preferable. R^2 are the same or different aryl groups having from 6 to 20 carbons or aralkyl groups having from 7 to 20 carbons. 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. In addition, R^3 is an alkenyl group having from 2 to 12 carbons, 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, of these, vinyl groups are preferable. R^4 are the same or different 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 groups described for R^1. Examples of the alkenyl group of R^4 include the same groups described for R^3.

[0015] In addition, in the formula, "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 $a+b+c=1$, preferably numbers satisfying $0.05 \leq a \leq 0.5$, $0 \leq b \leq 0.5$, $0.4 \leq c < 0.85$, and $a+b+c=1$, and even more preferably numbers satisfying $0.05 \leq a \leq 0.4$, $0 \leq b \leq 0.4$, $0.45 \leq c < 0.8$, and $a+b+c=1$. This is because the gas permeability of the cured product is reduced when "a" is greater than or equal to the lower limit of the range described above, and the cured product has sufficient strength when "a" is less than or equal to the upper limit of the range described above. 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.

[0016] The organopolysiloxane for component (A) is expressed by the average unit formula described above but may also have siloxane units represented by the formula: $R^1{}_3SiO_{1/2}$, siloxane units represented by the formula: $R^1R^2{}_2SiO_{1/2}$, siloxane units represented by the formula: $R^1{}_2R^2SiO_{1/2}$, siloxane units represented by the formula: $R^1R^3{}_2SiO_{1/2}$, siloxane units represented by the formula: $R^1SiO_{3/2}$, or siloxane units represented by the formula: $SiO_{4/2}$ within a range that does not diminish the object of the present invention. In the formulas, R^1 is an alkyl group having from 1 to 12 carbons, and examples thereof are the same as the groups described above. Further, in the formulas, R^2 is an aryl group having from 6 to 20 carbons or an aralkyl group having from 7 to 20 carbons, and examples thereof are the same as the groups described above. In the formulas, R^3 is an alkenyl group having from 2 to 12 carbons, and examples thereof are the same as the groups described above. The organopolysiloxane may also have silicon-bonded alkoxy group such as methoxy groups, ethoxy groups, and propoxy groups or silicon-bonded hydroxyl groups within a range that does not diminish the object of the present invention.

[0017] An example of a method of preparing such an organopolysiloxane is a method of hydrolyzing/condensing, in the presence of an acid or an alkali, a silane compound represented by the following general formula (I):

R^2SiX_3

a disiloxane represented by the following general formula (II-1):

$R^1R^2R^3SiOSiR^1R^2R^3$

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

$R^1R^2R^3SiX$.

[0018] The silane compound represented by the following general formula (I):

R^2SiX_3

is a raw material for introducing siloxane units represented by the formula: $R^2SiO_{3/2}$ into the organopolysiloxane. In the formulas, R^2 is an aryl group having from 6 to 20 carbons or an aralkyl group having from 7 to 20 carbons, examples thereof are synonymous with the groups described above. Of these, phenyl groups or naphthyl groups are preferable. Further, in the formulas, X is an alkoxy group, an acyloxy group, a halogen atom, or a hydroxyl group. Examples of the alkoxy group of X include a methoxy group, an ethoxy group, and a propoxy group. Examples of the acyloxy group of X include an acetoxy group. Examples of the halogen atom of X include a chlorine atom, and a bromine atom.

[0019] Examples of such a silane compound include alkoxy silanes such as phenyl trimethoxysilane, naphthyl trimethoxysilane, anthracenyl trimethoxysilane, phenanthryl trimethoxysilane, pyrenyl trimethoxysilane, phenyl triethoxysilane, naphthyl triethoxysilane, anthracenyl triethoxysilane, phenanthryl triethoxysilane, and pyrenyl triethoxysilane; acyloxysilanes such as phenyl triacetoxysilane, naphthyl triacetoxysilane, anthracenyl triacetoxysilane, phenanthryl triacetoxysilane, and pyrenyl triacetoxysilane; halosilanes such as phenyl trichlorosilane, naphthyl trichlorosilane, anthracenyl trichlorosilane, phenanthryl trichlorosilane, and pyrenyl trichlorosilane; and hydroxysilanes such as phenyl trihydroxysilane, naphthyl trihydroxysilane, anthracenyl trihydroxysilane, phenanthryl trihydroxysilane, and pyrenyl trihydroxysilane.

[0020] The disiloxane represented by the following general formula (II-1):

$R^1R^2R^3SiOSiR^1R^2R^3$

is a raw material for introducing siloxane units represented by the formula: $R^1R^2R^3SiO_{1/2}$ into the organopolysiloxane. In the formulas, R^1 is an alkyl group having from 1 to 12 carbons, examples thereof are synonymous with the groups described above, and, of these, methyl groups are preferable. Further, in the formulas, R^2 is an aryl group having from 6 to 20 carbons or an aralkyl group having from 7 to 20 carbons, examples thereof are synonymous with the groups described above, and, of these, phenyl groups or naphthyl groups are preferable. In the formulas, R^3 is an alkenyl group having from 2 to 12 carbons, examples thereof are synonymous with the groups described above, and, of these, vinyl groups are preferable.

[0021] An example of such a disiloxane is 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane.

[0022] The silane compound represented by the following general formula (II-2):

$$R^1R^2R^3SiX$$

is also a raw material for introducing siloxane units represented by the formula: $R^1R^2R^3SiO_{1/2}$ into the organopolysiloxane. In the formulas, R^1 is an alkyl group having from 1 to 12 carbons, examples thereof are synonymous with the groups described above, and, of these, methyl groups are preferable. Further, in the formulas, R^2 is an aryl group having from 6 to 20 carbons or an aralkyl group having from 7 to 20 carbons, examples thereof are synonymous with the groups described above, and phenyl groups or naphthyl groups are preferable. In the formulas, R^3 is an alkenyl group having from 2 to 12 carbons, examples thereof are synonymous with the groups described above, and, of these, vinyl groups are preferable. Moreover, in the formulas, X is an alkoxy group, an acyloxy group, a halogen atom, or a hydroxyl group; and examples thereof are the same as the groups described above.

[0023] Examples of such a silane compound include alkoxysilanes such as methylphenylvinylmethoxysilane and methylphenylvinylethoxysilane; acetoxysilanes such as methylphenylvinylacetoxysilane; chlorosilanes such as methylphenylvinylchlorosilane; and hydroxysilanes such as methylphenylvinylhydroxysilane.

[0024] In the preparation method described above, a silane compound or cyclic silicone compound for introducing siloxane units represented by the formula: $R^4{}_2SiO_{2/2}$ or a silane compound or silane oligomer for introducing siloxane units represented by the formula: $R^1{}_3SiO_{1/2}$, siloxane units represented by the formula: $R^1R^2{}_2SiO_{1/2}$, siloxane units represented by the formula: $R^1{}_2R^2SiO_{1/2}$, siloxane units represented by the formula: $R^1R^3{}_2SiO_{1/2}$, siloxane units represented by the formula: $R^1SiO_{3/2}$, or siloxane units represented by the formula: $SiO_{4/2}$ may be reacted with the organopolysiloxane as necessary. In the formulas, R^1 is an alkyl group having from 1 to 12 carbons, and examples thereof are the same as the groups described above. Further, in the formulas, R^2 is an aryl group having from 6 to 20 carbons or an aralkyl group having from 7 to 20 carbons, and examples thereof are the same as the groups described above. In the formulas, R^3 is an alkenyl group having from 2 to 12 carbons, and examples thereof are the same as the groups described above. In the formulas, R^4 are the same or different alkyl groups having from 1 to 12 carbons, alkenyl groups having from 2 to 12 carbons, or phenyl groups, and examples thereof are the same as the groups described above.

[0025] Examples of such a silane compound include alkoxysilanes such as dimethyldimethoxysilane, dimethyldiethoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, methylvinyldimethoxysilane, methylvinyldiethoxysilane, phenylvinyldimethoxysilane, phenylvinyldiethoxysilane, trimethylmethoxysilane, trimethylethoxysilane, methyldiphenylmethoxysilane, methyldiphenylethoxysilane, methyltrimethoxysilane, tetramethoxysilane, and tetraethoxysilane; acetoxysilanes such as dimethyldiacetoxysilane, methylphenyldiacetoxysilane, diphenyldiacetoxysilane, methylvinyldiacetoxysilane, phenylvinyldiacetoxysilane, trimethylacetoxysilane, methyldiphenylacetoxysilane, methyltriacetoxysilane, and tetraacetoxysilane; halosilanes such as dimethyldichlorosilane, diethyldichlorosilane, methylphenyldichlorosilane, diphenyldichlorosilane, methylvinyldichlorosilane, phenylvinyldichlorosilane, trimethylchlorosilane, methyldiphenylchlorosilane, methyltrichlorosilane, and tetrachlorosilane; and hydroxysilanes such as dimethyldihydroxysilane, diethyldihydroxysilane, methylphenyldihydroxysilane, diphenyldihydroxysilane, methylvinyldihydroxysilane, trimethylhydroxysilane, methyldiphenylhydroxysilane, and methyltrihydroxysilane. Examples of such a cyclic silicone compound include cyclic dimethylsiloxane oligomers, cyclic phenylmethylsiloxane oligomers, and cyclic diphenylsiloxane oligomers. Further, examples of silane oligomers include partial hydrolysates of tetramethoxysilane and partial hydrolysates of tetraethoxysilane.

[0026] The preparation method described above is characterized in that the silane compound (I), the disiloxane (II-1) and/or the silane compound (II-2), and other silane compounds, cyclic silicone compounds, or silane oligomers, if necessary, are hydrolyzed/condensed in the presence of an acid or an alkali.

[0027] Acids that may be used are exemplified by hydrochloric acid, acetic acid, formic acid, nitric acid, oxalic acid, sulfuric acid, phosphoric acid, polyphosphoric acid, polycarboxylic acid, trifluoromethane sulfonic acid, and ion exchange resins. Further, the utilized base is exemplified by inorganic bases such as potassium hydroxide, sodium hydroxide, and the like; and organic base compounds such as triethylamine, diethylamine, monoethanolamine, diethanolamine, triethanolamine, ammonia water, tetramethylammonium hydroxide, alkoxysilanes having an amino group, aminopropyltrimethoxysilane, and the like.

[0028] Furthermore, an organic solvent may be used in the preparation method. The utilized organic solvent is exemplified by ethers, ketones, acetates, aromatic or aliphatic hydrocarbons, and a γ-butyrolactone; and mixtures of two or more types of such solvents. Preferred organic solvents are exemplified by propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, propylene glycol mono-t-butyl ether, γ-butyrolactone, toluene, and xylene.

[0029] In order to accelerate the hydrolysis and condensation reaction of each of the components in the preparation method, water or a mixed solution of water and alcohol is preferably added. Methanol and ethanol are preferred examples of the alcohol. This reaction is promoted by heating, and if an organic solvent is used, the reaction is preferably performed at the reflux temperature of the organic solvent.

[0030] Component (B), which is an optional component for imparting the cured product with softness, extensibility, and flexibility, is a straight-chain organopolysiloxane having at least two alkenyl groups and not having any silicon-bonded hydrogen atoms in a molecule. Examples of the alkenyl groups in component (B) include alkenyl groups having from 2 to 12 carbons 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. Of these, vinyl groups are preferable. Examples of groups bonding to silicon atoms other than alkenyl groups in component (B) include alkyl groups having from 1 to 12 carbons 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 carbons 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 and ethyl groups, alkoxy groups such as methoxy groups and ethoxy groups, or halogen atoms such as chlorine atoms and bromine atoms; aralkyl groups having from 7 to 20 carbons such as 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; and halogenated alkyl groups having from 1 to 12 carbons such as chloromethyl groups and 3,3,3-trifluoropropyl groups. Of these, methyl groups and phenyl groups are preferable.

[0031] Examples of such component (B) include copolymers of dimethylsiloxane and methylvinylsiloxane capped at both molecular terminals with trimethylsiloxy groups, methylvinylpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, copolymers of dimethylsiloxane, methylvinylsiloxane, and methylphenylsiloxane 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, copolymers of dimethylsiloxane and methylvinylsiloxane capped at both molecular terminals with dimethylvinylsiloxy groups, copolymers of dimethylsiloxane, methylvinylsiloxane, and methylphenylsiloxane capped at both molecular terminals with dimethylvinylsiloxy groups, and mixtures of two or more types of these organopolysiloxanes.

[0032] The content of component (B) in this composition is in the range of 0 to 70 mass%, preferably in the range of 0 to 50 mass%, and particularly preferably in the range of 0 to 40 mass% with respect to this composition. This is because when the content of component (B) is less than or equal to the upper limit of the range described above, it is possible to impart the cured product with softness, extensibility, and flexibility without increasing the gas permeability of the cured product, thus making it possible to improve the reliability of an optical semiconductor device produced using this composition.

[0033] Component (C) is a crosslinking agent of the present composition and is an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in a molecule, and at least 80 mass% of this component comprising an organotrisiloxane represented by the following formula:

$$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H.$$

This is because, when the organotrisiloxane described above is used as a crosslinking agent, the compound has good reactivity to component (A) described above, which makes it possible to rapidly cure the composition. In addition, an organotrisiloxane such as that described above is able to reduce the viscosity of the composition and to enhance the handleability of the composition.

[0034] Component (C) has at least 80 mass% of the organotrisiloxane described above, and the other organopolysiloxanes are not particularly limited as long as there are at least two silicon-bonded hydrogen atoms in a molecule. Such an organopolysiloxane may have a straight, branched, cyclic, net-like, or a partially branched straight-chain molecular structure. Examples of other groups bonding to silicon atoms in this organopolysiloxane include alkyl groups having from 1 to 12 carbons, aryl groups having from 6 to 20 carbons, aralkyl groups having from 7 to 20 carbons, and halogenated alkyl groups having from 1 to 12 carbons. Examples of these groups include the same groups as those described above, and methyl groups and phenyl groups are preferable.

[0035] The other organopolysiloxane is exemplified by a methylhydrogenpolysiloxane capped at both molecular terminals with trimethylsiloxy groups, a copolymer of dimethylsiloxane and methylhydrogensiloxane capped at both molecular terminals with trimethylsiloxy groups, a copolymer of dimethylsiloxane, methylhydrogensiloxane and methylphenylsiloxane capped at both molecular terminals with trimethylsiloxy groups, a dimethylpolysiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, a copolymer of dimethylsiloxane and methylphenylsiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, a methylphenylpolysiloxane capped at both molecular terminals with dimethylhydrogensiloxy groups, organopolysiloxane copolymers composed of siloxane units represented by the general formula: $R'_3SiO_{1/2}$ and siloxane units represented by the general formula: $R'_2HSiO_{1/2}$ and siloxane units represented by the formula: $SiO_{4/2}$, organopolysiloxane copolymers composed of siloxane units represented by the general formula: $R'_2HSiO_{1/2}$ and siloxane units represented by the formula: $SiO_{4/2}$, organopolysiloxane copolymers composed of siloxane units represented by the general formula: $R'HSiO_{2/2}$, and siloxane units represented by the general formula: $R'SiO_{3/2}$ or siloxane units represented by the formula: $HSiO_{3/2}$, and mixtures of two or more such organopolysiloxanes. In the formulas, R' is an alkyl group having from 1 to 12 carbons, an aryl group having from 6 to 20 carbons, an aralkyl group having from 7 to 20 carbons, or a halogenated alkyl group having from 1 to 12 carbons, and examples thereof are the same as the groups described above.

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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 unsubstituted monovalent hydrocarbon groups such as alkyl groups, alkenyl groups, aryl groups, aralkyl groups, and halogenated alkyl groups; epoxy-containing monovalent organic groups such as 3-glycidoxypropyl groups, 4-glycidoxybutyl groups, or similar glycidoxyalkyl groups; 2-(3,4-epoxycyclohexyl)ethyl groups, 3-(3,4-epoxycyclohexyl)propyl groups, or similar epoxycyclohexylalkyl groups; or 4-oxiranylbutyl groups, 8-oxiranyloctyl groups, or similar oxiranylalkyl groups; acrylic group-containing monovalent organic groups such as 3-methacryloxypropyl groups; and hydrogen atoms. 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 straight structure, partially branched straight structure, branched chain structure, cyclic structure, and net-like structure. A straight chain structure, branched chain structure, and net-like structure are particularly preferred. This type of organosilicon compound is exemplified by silane compounds such as 3-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and the like; siloxane compounds having at least one of silicon-bonded alkenyl groups or 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 in a moulecule and a siloxane compound having at least one silicon-bonded hydroxyl group or 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 this 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 components (A) to (D) described above.

[0040] A reaction inhibitor, for example, an alkyne alcohol such as 2-methyl-3-butyn-2-ol, 3,5-dimethyl-1-hexyn-3-ol and 2-phenyl-3-butyn-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.

[0041] 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 CASN 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.

[0042] Moreover, an inorganic filler such as silica, glass, alumina, zinc oxide and the like; 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.

[0043] 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.

[0044] The cured product of the present invention will now be described in detail.

[0045] 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.

[0046] The optical semiconductor device of the present invention will now be explained in detail.

[0047] 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.

[0048] 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 frame material 5 is provided around this LED chip 1, and the LED chip 1 inside the frame material 5 is sealed by a cured product 6 of the curable silicone composition of the present invention.

[0049] 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 frame 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

[0050] 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 examples. The viscosity is the value at 25°C. The characteristics of the curable silicone composition, the cured product thereof, and the optical semiconductor device were measured as follows.

[0051]

[Evaluation of curability]

The curing rate of the curable silicone composition was evaluated based on the heat generation peak temperature (°C) measured at a heating rate of 10°C/min using a differential scanning calorimeter (DSC7000; manufactured by SII Nanotechnology Inc.) and the time (seconds) required for the torque value to reach 1 dNm when measured at a measurement temperature of 150°C and a die deflection angle of 1° using a curastometer (RHEOMETER MDR2000; manufactured by Alpha Technologies Co., Ltd.).

[0052]

[Water vapor permeability of the cured product]

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.

[0053]

[Reliability of the optical semiconductor device]

The optical semiconductor device illustrated in Figure 1 was produced by heating the curable silicone composition for 2 hours at 150°C. This optical semiconductor device was subjected to 24-hour exposure tests under conditions with a temperature of 50°C, 75% relative humidity, and a hydrogen sulfide gas concentration of 20 ppm. The reliability of the optical semiconductor device was evaluated by measuring changes in the luminous efficiency of the optical semiconductor device before and after the exposure tests.

[0054]

[Synthesis Example 1]

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 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 adding 0.68 g (11.4 mmol) of acetic acid. The generated salt was removed by filtration. The low boiling point substances were removed from the obtained transparent solution by heating under vacuum to obtain 347 g (98% yield) of a colorless transparent gum-like viscous liquid.

[0055] As a result of nuclear magnetic resonance spectroscopy, it was observed that this liquid was an organopolysiloxane represented by the following average unit formula:

$[(CH_3)(C_6H_5)CH_2{=}CHSiO_{1/2}]_{0.23}(C_6H_5SiO_{3/2})_{0.77}$.

The mass average molecular weight (Mw) of this organopolysiloxane was 1,617, and the dispersity (Mw/Mn) was 1.16.

[0056]

[Practical Example 1]

A curable silicone composition with a viscosity of 8,300 mPa·s was prepared by mixing 77.9 parts by mass of the organopolysiloxane prepared in Synthesis Example 1, 21.9 parts by mass of an organotrisiloxane represented by the following formula:

$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 1 mol per 1 mol of the vinyl groups in the organopolysiloxane described above), and 0.2 parts by mass of a 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (containing 0.1 mass% of platinum).

[0057] The time required for this curable silicone composition to reach a torque value of 1 dNm was 36 seconds, and the DSC heat generation peak temperature was 122°C. The water vapor permeability of the cured product was 6.7 $g/m^2 \cdot 24h$.

[0058]

[Practical Example 2]

A curable silicone composition with a viscosity of 4,300 mPa·s was prepared by mixing 64.7 parts by mass of the organopolysiloxane prepared in Synthesis Example 1, 15.2 parts by mass of a methylphenylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups having a viscosity of 3,000 mPa·s, 20.0 parts by mass of an organotrisiloxane represented by the following formula:

$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 1 mol per 1 mol of the vinyl groups in the organopolysiloxane and the methylphenylpolysiloxane described above), and 0.2 parts by mass of a 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (containing 0.1 mass% of platinum).

[0059] The time required for this curable silicone composition to reach a torque value of 1 dNm was 44 seconds, and the DSC heat generation peak temperature was 120°C. The water vapor permeability of the cured product was 7.8 $g/m^2 \cdot 24h$.

[0060]

[Practical Example 3]

A curable silicone composition with a viscosity of 11,500 mPa·s was prepared by mixing 76.3 parts by mass of the organopolysiloxane prepared in Synthesis Example 1, 20.0 parts by mass of an organotrisiloxane represented by the following formula:

$$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H$$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 0.9 mol per 1 mol of the vinyl groups in the organopolysiloxane described above), 3.5 parts by mass of an organopolysiloxane represented by the following average formula:

$$H(CH_3)_2SiO(C_6H_5)_{2.5}SiOSi(CH_3)_2H$$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 0.1 mol per 1 mol of the vinyl groups in the organopolysiloxane described above), and 0.2 parts by mass of a 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (containing 0.1 mass% of platinum).

[0061] The time required for this curable silicone composition to reach a torque value of 1 dNm was 56 seconds, and the DSC heat generation peak temperature was 122°C. The water vapor permeability of the cured product was 6.5 $g/m^2 \cdot 24h$.

[0062]

[Practical Example 4]

A curable silicone composition with a viscosity of 10,600 mPa·s was prepared by mixing 77.8 parts by mass of the organopolysiloxane prepared in Synthesis Example 1, 18.7 parts by mass of an organopolysiloxane represented by the following formula:

$$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H$$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 0.72 mol per 1 mol of the vinyl groups in the organopolysiloxane described above), 3.3 parts by mass of an organotrisiloxane represented by the following average unit formula:

$$(C_6H_5SiO_{3/2})_{0.4}\,[(CH_3)_2HSiO_{1/2}]_{0.6}$$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 0.28 mol per 1 mol of the vinyl groups in the organopolysiloxane described above), and 0.2 parts by mass of a 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (containing 0.1 mass% of platinum).

[0063] The time required for this curable silicone composition to reach a torque value of 1 dNm was 16 seconds, and the DSC heat generation peak temperature was 110°C. The water vapor permeability of the cured product was 6.6 $g/m^2 \cdot 24h$.

[0064]

[Comparative Example 1]

A curable silicone composition with a viscosity of 28,500 mPa·s was prepared by mixing 65.2 parts by mass of the organopolysiloxane prepared in Synthesis Example 1, 34.8 parts by mass of an organopolysiloxane represented by the following average formula:

$$H(CH_3)_2SiO(C_6H_5)_{2.5}SiOSi(CH_3)_2H$$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 1 mol per 1 mol of the vinyl groups in the organopolysiloxane described above), and 0.2 parts by mass of a 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (containing 0.1 mass% of platinum).

[0065] The time required for this curable silicone composition to reach a torque value of 1 dNm was 166 seconds, and the DSC heat generation peak temperature was 133°C. The water vapor permeability of the cured product was 6.3 $g/m^2 \cdot 24h$.

[0066]

[Comparative Example 2]

A curable silicone composition with a viscosity of 12,300 mPa·s was prepared by mixing 53.6 parts by mass of the organopolysiloxane prepared in Synthesis Example 1, 15.2 parts by mass of a methylphenylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups having a viscosity of 3,000 mPa·s, 31.2 parts by mass of an organopolysiloxane represented by the following average formula:

$$H(CH_3)_2SiO(C_6H_5)_{2.5}SiOSi(CH_3)_2H$$

(in an amount that the amount of silicon-bonded hydrogen atoms in this component is 1 mol per 1 mol of the vinyl groups in the organopolysiloxane and the methylphenylpolysiloxane described above), and 0.2 parts by mass of a 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane solution of a platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (containing 0.1 mass% of platinum).

[0067] The time required for this curable silicone composition to reach a torque value of 1 dNm was 211 seconds, and the DSC heat generation peak temperature was 130°C. The water vapor permeability of the cured product was 7.4 $g/m^2 \cdot 24h$.

[0068] As a result of a comparison of Practical Example 1 and Comparative Example 1 and a comparison of Practical Example 2 and Comparative Example 2, it was observed that when an organotrisiloxane represented by the following formula:

$$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H$$

is used as a crosslinking agent, the viscosity of the curable silicone composition decreases, and the curing rate increases.

[0069]

[Practical Example 5]

An optical semiconductor device was created using the curable silicone composition prepared in Practical Example 1. When the reliability of this optical semiconductor device was evaluated, no changes in luminous efficiency of the optical semiconductor device were observed before and after exposure tests.

Industrial Applicability

[0070] The curable silicone composition of the present invention can be used as an adhesive, a potting agent, a protective agent, a coating agent, or an underfill agent for electrical/electronic use. In particular, the curable silicone composition has excellent handleability and high reactivity and can form a cured product with low gas permeability, so the composition is suitable as a sealing agent or a protective coating material for an optical semiconductor element in an optical semiconductor device such as a light-emitting diode (LED).

Description of Symbols

[0071]

1	Optical semiconductor element
2	Lead frame

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

CLAIMS

1. A curable silicone composition comprising:

(A) an organopolysiloxane having at least two alkenyl groups in a molecule and represented by the following average unit formula:

$$(R^1R^2R^3SiO_{1/2})_a(R^4{}_2SiO_{2/2})_b(R^2SiO_{3/2})_c$$

wherein, R^1 is an alkyl group having from 1 to 12 carbons; R^2 are the same or different aryl groups having from 6 to 20 carbons or aralkyl groups having from 7 to 20 carbons; R^3 is an alkenyl group having from 2 to 12 carbons; R^4 are the same or different alkyl groups having from 1 to 12 carbons, alkenyl groups having from 2 to 12 carbons, or phenyl groups; 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 $a+b+c=1$;

(B) a straight-chain organopolysiloxane having at least two alkenyl groups and not having any silicon-bonded hydrogen atoms in a molecule, in 0 to 70 mass% of this composition;

(C) an organopolysiloxane having at least two silicon-bonded hydrogen atoms in a molecule, and at least 80 mass% of this component comprising an organotrisiloxane represented by the following formula:

$$H(CH_3)_2SiO(C_6H_5)_2SiOSi(CH_3)_2H,$$

in an amount that the amount of silicon-bonded hydrogen atoms in this component is from 0.1 to 5 mol per 1 mol of total alkenyl groups in components (A) and (B); and

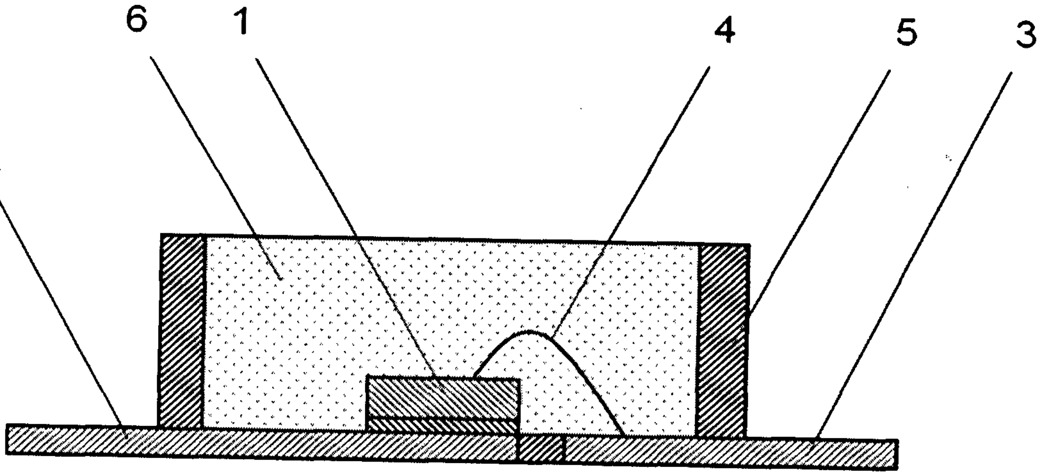
(D) an effective amount of a hydrosilylation reaction catalyst.

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

3. A cured product produced by curing the curable silicone composition described in claim 1 or 2.

4. An optical semiconductor device, wherein an optical semiconductor element is sealed by a cured product of the curable silicone composition described in claim 1 or 2.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2013/079333

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D183/04 C08G77/50 H01L23/29
ADD.

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)
C09D C08G H01L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/056236 A1 (HAMAMOTO YOSHIHIRA [JP] ET AL) 8 March 2012 (2012-03-08) example 3; table 1 paragraph [0002] -----	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bergmeier, Martin

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2013/079333

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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