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(71) Applicant (*for all designated States except US*): **DOW CORNING TORAY SILICONE CO., LTD.** [JP/JP]; 1-3, Maurnouchi 1-chome, Chiyoda-ku, Tokyo 100-0005 (JP).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **YAMAKAWA, Kimio** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusakaigan, Ichihara-shi, Chiba 299-0108 (JP). **NAKAYOSHI, Kazumi** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusakaigan, Ichihara-shi, Chiba 299-0108 (JP). **ISHIKAWA, Hiroki** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusakaigan, Ichihara-shi, Chiba 299-0108 (JP). **MINE, Katsutoshi** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba 299-0108 (JP).

(74) Agent: **KUBOTA, Yoshitake**; c/o ASA International Patent Firm Chiba Office, 43-27 Satsukigaoka 1-chome, Hanamigawa-ku, Chiba-shi, Chiba 262-0014 (JP).

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(54) Title: THERMOCONDUCTIVE FILLER, THERMOCODUCTIVE SILICONE ELASTOMER COMPOSITION, AND SEMICONDUCTOR DEVICES

(57) Abstract: A thermoconductive filler whose surface has been treated or coated with a fatty acid and thereafter has also been treated or coated with an epoxy-functional compound and a curing catalyst for epoxy resins. A thermoconductive silicone elastomer compositions that contains the thermoconductive filler whose surface has been treated or coated with a fatty acid and thereafter has also been treated or coated with an epoxy-functional compound and a curing catalyst for epoxy resins. A semiconductor device afforded by coating a semiconductor chip with the thermoconductive silicone elastomer composition and curing.

DESCRIPTION

THERMOCONDUCTIVE FILLER, THERMOCONDUCTIVE SILICONE ELASTOMER COMPOSITION, AND SEMICONDUCTOR DEVICES

5

Technical Field

[0001] This invention relates to thermoconductive fillers, thermoconductive silicone elastomer compositions, and semiconductor devices. More particularly, this invention relates to a thermoconductive filler whose surface has been treated or coated with a fatty acid
10 and thereafter has also been treated or coated with an epoxy-functional compound and a curing catalyst for epoxy resins. This invention further relates to thermoconductive silicone elastomer compositions that contain said thermoconductive filler, and to semiconductor devices afforded by coating a semiconductor chip with such a thermoconductive silicone elastomer composition and curing.

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Background

[0002] Fluid thermoconductive silicone elastomer compositions that contain a thermoconductive filler, such as a thermally conductive inorganic material or a metal, are used as heat-dissipating adhesives, potting agents, and protective coatings for electrical and electronic components. Fluid hydrosilylation-curing silicone elastomer compositions whose
20 essential components are

a fluid organopolysiloxane bearing Si-bonded alkenyls,

a fluid organopolysiloxane bearing Si-bonded hydrogen atoms,

a hydrosilylation catalyst, and

a thermoconductive filler

are disclosed in, for example, Japanese Unexamined Patent Application Publication (Kokai) Numbers Hei 2-97559 (97,559/1990) and Hei 2-41362 (41,362/1990). These fluid thermoconductive silicone elastomer compositions cure to give low-stress elastomers that exhibit an excellent heat resistance and thermal conductivity and as a result are used as heat-dissipating adhesives, potting agents, and protective coatings for electrical and electronic components. They are used in particular as adhesives for bonding semiconductor chips to a heat-dissipating sheet or plate. These thermoconductive silicone elastomer compositions are in some cases filled with a metal thermoconductive filler to obtain higher levels of thermal conductivity. An electroconductive hydrosilylation-curing organopolysiloxane composition filled with large amounts of silver powder is disclosed in Japanese Unexamined Patent Application Publication (Kokai) No. Hei 2-238054 (238,054/1990). This composition also exhibits excellent thermal conductivity; however, commercial silver powder retains a fatty acid used as a lubricant during its production, which results in a particle surface that has become coated or treated by the fatty acid. The admixture of such silver powder into a silicone elastomer composition does lead to an improved thermal conductivity by the cured product afforded by the composition, but also results in a substantial decline in the thermal stability of this cured product and in a substantial deterioration of the reliability of semiconductors devices that employ such a cured product. These problems are also similarly caused by thermoconductive fillers other than silver powder.

[0003] The object of this invention is to provide a thermoconductive filler that, when blended in a silicone elastomer composition, does not impair the thermal stability of the cured product afforded by said composition. A further object of this invention is to provide a thermoconductive silicone elastomer composition whose cured product exhibits an excellent thermal stability. A further object of this invention is to provide highly reliable

semiconductor devices as afforded by coating a semiconductor chip with the aforementioned composition and curing.

Summary of the Invention

5 **[0004]** The problems described above may be eliminated by a thermoconductive filler afforded by subjecting a thermoconductive filler whose surface has been treated or coated with a fatty acid to further treatment or coating with an epoxy-functional compound and a curing catalyst for epoxy resins, a thermoconductive silicone elastomer composition containing the aforementioned thermoconductive filler, and a semiconductor device as
10 characteristically afforded by coating a semiconductor chip with the aforementioned thermoconductive silicone elastomer composition and curing.

[0005] This invention relates to

(1) thermoconductive fillers whose surface has been treated or coated with a fatty acid and thereafter has also been treated or coated with an epoxy-functional compound and
15 a curing catalyst therefor,

(2) thermoconductive silicone elastomer compositions that characteristically contain the thermoconductive filler whose surface has been treated or coated with a fatty acid and thereafter has also been treated or coated with an epoxy-functional compound and a curing catalyst for epoxy resins, and

20 (3) semiconductor devices as characteristically afforded by coating a semiconductor chip with the aforementioned thermoconductive silicone elastomer composition and curing.

Brief Description of Drawing

[0006] Figure 1 illustrates the cross section of an LSI that is one example of the inventive semiconductor device.

Reference symbols

1 semiconductor chip

5 2 substrate for circuit

3 wiring

4 gold bumps

5 thermoconductive silicone rubber

6 heat-dissipating plate

10

Detailed Description of the Preferred Embodiments

[0007] The inventive thermoconductive filler is characterized in that the surface of a thermoconductive filler (b) has been treated or coated with a fatty acid (a) and thereafter has also been treated or coated with an epoxy-functional compound (c) and a curing catalyst (d)
15 for epoxy resins. The fatty acid (a) used to treat the surface of the thermoconductive filler (b) is not critical and may be a saturated fatty acid or an unsaturated fatty acid. The fatty acid (a) preferably contains at least 6 carbon atoms and more preferably at least 10 carbon atoms in consideration of its lubricating performance during the production phase. Examples of fatty acids that contain at least 6 carbon atoms are oleic acid, linoleic acid,
20 linolenic acid, lauric acid, palmitic acid, stearic acid, myristic acid, and naphthenic acid. A higher fatty acid containing at least ten carbon atoms is preferable as the fatty acid (a). The thermoconductive filler (b) can be treated or coated with the fatty acid (a) by kneading or stirring the two materials in a mixer or by impregnating the thermoconductive filler (b) with a solution of the fatty acid (a) and then evaporating the solvent.
25 [0008] The material composing the thermoconductive filler (b) should not inhibit the cure of the silicone elastomer composition and can be exemplified by metal fillers such as gold, silver, copper, aluminum, nickel, palladium, solder, brass, and shape-memory alloys; inorganic fillers such as crystalline silica, glass, silicon nitride, boron nitride, silicon carbide, carbon black, and diamond; and fillers comprising metal compounds, such as aluminum

nitride, alumina, titanium oxide, aluminum hydroxide, and aluminum sulfide and their composites. A thermoconductive filler (b) whose surface has been treated or coated with a fatty acid during production of the thermoconductive filler (b) itself is optimal as the thermoconductive filler (b) whose surface has been treated or coated with a fatty acid and thereafter has also been treated or coated with an epoxy-functional compound and a curing catalyst for epoxy resins.

Metal fillers, of which silver is a typical example, are an example of thermoconductive fillers (b) that are treated with the fatty acid. The silver can be selected without restriction from reduced silver, atomized silver, and electrolytic silver. The shape of the thermoconductive filler (b) is not critical as long as it is granular or particulate and can be exemplified by ground, spherical, fibrous, columnar, flake, sheets, plates, and coil. The particle size should be that ordinarily exhibited by thermoconductive fillers, but is not otherwise critical. As a general matter, the maximum particle size will be no greater than 200 micrometers (μm) and the average particle size will be from 0.1 to 50 μm (excluding the case of carbon black). For carbon black, particle size depends on the type of carbon black selected. For example, particle size for carbon black may be 11 to 19 nanometers (nm) for N110(SAF) and N195(SCF), up to 201－500 nm for N907(NT-NS) and N990(MT).

[0009] The epoxy-functional compound (c) used to treat or coat the fatty acid-treated or -coated thermoconductive filler should be an organic compound that contains at least one epoxy group in the molecule, but is not otherweise critical. Typical examples of the epoxy group are the epoxy groups in the glycidoxyalkyl, epoxyalkyl, and 3,4-epoxycyclohexyl groups. The epoxy-functional compound (c) can be a monomolecular compound, oligomer, or polymer and can be a solid or liquid at ambient temperature. If the epoxy-functional compound (c) is a solid at ambient temperature, it is preferably heat-fusible or soluble in an organic solvent. The epoxy-functional compound (c) can be exemplified by bisphenol-type epoxy resins, biphenyl-type epoxy resins, novolac-type epoxy resins, alicyclic epoxy resins, epoxy-functional organosilanes, epoxy-functional organosiloxane oligomers, epoxy- and alkoxy-functional organosiloxane oligomers, epoxy-functional organopolysiloxanes, and epoxy-modified silicones. Based on a consideration of the affinity with the silicone

elastomer composition, the epoxy-functional compound (c) is preferably an organosilane, organosiloxane oligomer, organopolysiloxane, or epoxy-functional silicone, in each case containing at least one epoxy group.

[0010] The curing catalyst (d) for epoxy resins (this catalyst is referred to below simply as the curing catalyst) is not critical as long as it is a compound that can be used in combination with a curing agent (e.g., polyamines, polyaminoamides, dicyandiamide, polycarboxylic acids, polycarboxylic acid anhydrides, phenolic resins, novolac resins, and polyols) for epoxy resins to accelerate curing. The curing catalyst (d) can be exemplified by tertiary amines, quaternary ammonium salts, imidazoles, boron compounds, phosphine, and organometal compounds (e.g., organometal complex salts, organozirconium compounds, and organoaluminum compounds), but preferably is a compound that does not inhibit the hydrosilylation reaction, such as organometal compounds. The curing catalyst (d) is preferably an organometal compound and particularly preferably an organoaluminum compound or organoaluminum chelate compound when it is used in combination with an epoxy-functional organosilane, epoxy-functional organosiloxane oligomer, epoxy-functional organopolysiloxane, or epoxy-modified silicone. The curing catalyst (d) can also be used in combination with a curing agent for epoxy resins, such as a polyamine, polyaminoamide, dicyandiamide, polycarboxylic acid, polycarboxylic acid anhydride, phenolic resin, novolac resin, or polyol.

[0011] The surface of the thermoconductive filler (b) may be treated or coated with the fatty acid during production of the fatty acid-treated or coated thermoconductive filler. The following methods, for example, can be used to effect treatment or coating with the epoxy-functional compound (c) and the curing catalyst (d) of the thermoconductive filler whose surface has been treated or coated with the fatty acid (a):

(i) dry-treatment methods in which the fatty acid-treated or coated thermoconductive filler, epoxy-functional compound, and curing catalyst are reacted by intermixing,

(ii) wet-treatment methods in which the fatty acid-treated or coated thermoconductive filler, epoxy-functional compound, and curing catalyst are reacted by intermixing in a solvent and the solvent is thereafter removed, and

(iii) in-situ treatment methods in which the fatty acid-treated or coated thermoconductive filler, epoxy-functional compound, and curing catalyst are reacted by intermixing in a vinyl-functional organopolysiloxane that will be used as a component of the silicone elastomer composition.

In-situ treatment methods are preferred because they facilitate preparation of the thermoconductive silicone elastomer composition. The reaction in these treatment methods can be accelerated by the application of heat or ultrasonic vibration.

[0012] The inventive thermoconductive filler is useful as a thickener or filler that can impart thermal conductivity to, for example, curable silicone elastomer compositions, curable silicone resin compositions, and silicone oil compounds.

[0013] The thermoconductive silicone elastomer composition according to this invention characteristically contains the thermoconductive filler (b) whose surface has been treated or coated with a fatty acid (a) and thereafter has also been treated or coated with an epoxy-functional compound (c) and a curing catalyst (d). The content of this treated or coated thermoconductive filler will vary with the thermal conductivity and specific gravity of the thermoconductive filler and with the desired thermal conductivity and thus cannot easily be unconditionally specified. As a general matter, however, the composition will contain 9 to 98 weight % treated or coated thermoconductive filler and preferably contains 20 to 95 weight% treated or coated thermoconductive filler.

[0014] There are no particular limitations on the curing mechanism and properties of the silicone elastomer composition of this invention. Examples of this silicone elastomer composition are hydrosilylation-curing silicone elastomer compositions, organoperoxide-curing silicone elastomer compositions, and condensation-curing silicone elastomer compositions. Hydrosilylation-curing silicone elastomer compositions are preferred among the preceding for their rapidity and uniformity of cure. Among hydrosilylation-curing silicone elastomer compositions, those that are fluid or liquid at ambient temperature are preferred for their processing characteristics.

[0015] The essential components of such hydrosilylation-curing silicone elastomer compositions are

(A) an organopolysiloxane that contains at least two silicon-bonded alkenyl groups in each molecule,

(B) an organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule, and

(C) a hydrosilylation catalyst, and optionally

(D) a hydrosilylation inhibitor.

[0016] Component (A) undergoes crosslinking through the hydrosilylation reaction of its silicon-bonded alkenyl groups with the silicon-bonded hydrogen atoms in component (B). Component (B) preferably contains at least three silicon-bonded hydrogen atoms when component (A) contains two silicon-bonded alkenyl groups, while component (A) preferably contains at least three silicon-bonded alkenyl groups when component (B) contains two silicon-bonded hydrogen atoms. The alkenyl group can be exemplified by vinyl, allyl, butenyl, pentenyl, and hexenyl with vinyl being the most generally used.

[0017] The molecular structure of component (A) can be exemplified by straight chain, partially branched straight chain, branched chain, cyclic, and network. Straight chain and

partially branched straight chain molecular structures are optimal for obtaining an elastomer, *i.e.*, a rubber or gel, after curing. The silicon-bonded alkenyl groups in component (A) can be bonded in terminal or pendant position on the molecular chain or at both positions. The non-alkenyl silicon-bonded groups in component (A) can be exemplified by unsubstituted or
5 substituted monovalent hydrocarbyl groups, for example, alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl; aryl groups such as phenyl, tolyl, xylyl, and naphthyl; aralkyl groups such as benzyl and phenethyl; and halogenated alkyl groups such as 3-chloropropyl and 3,3,3-trifluoropropyl. Among these, methyl is the group most generally used because this facilitates industrial production, followed in terms of generality of use by
10 the use of both methyl and phenyl.

[0018] Viewed in terms of the handling and post-cure properties of the composition, the viscosity of component (A) at 25°C is preferably 10 to 1,000,000 milliPascal·seconds (mPa·s) and more preferably is 100 to 50,000 mPa·s. There is a tendency for the mechanical strength of the cured product to be unsatisfactory when component (A) has a viscosity below
15 this range. A component (A) viscosity above this range results in an increased viscosity for the composition that may impair its handling. However, component (A) can be a so-called gum.

[0019] Examples of component (A) include:
dimethylpolysiloxanes endblocked by dimethylvinylsiloxy at both terminals,
20 dimethylsiloxane-methylvinylsiloxane copolymers endblocked by dimethylvinylsiloxy at both terminals,
dimethylsiloxane-methylvinylsiloxane copolymers endblocked by trimethylsiloxy at both terminals,
straight-chain dimethylpolysiloxanes whose terminals are endblocked by dimethylvinylsiloxy
25 and trimethylsiloxy,

branched-chain methylpolysiloxanes whose terminals are endblocked by dimethylvinylsiloxy and trimethylsiloxy, and

polysiloxanes as afforded by replacing a portion of the methyl in the aforementioned polysiloxanes with phenyl.

5 Two or more types of component (A) can be used in combination.

[0020] Component (B) is a crosslinker for component (A), and it undergoes crosslinking through the hydrosilylation reaction of its silicon-bonded hydrogen atoms with the silicon-bonded alkenyl groups in component (A). Component (B) can have, for example, a straight-chain, partially branched straight-chain, branched-chain, or network molecular structure.

10 The silicon-bonded hydrogen atoms can be bonded in terminal or pendant position on the molecular chain or at both positions. The non-hydrogen silicon-bonded groups in component (B) can be exemplified by unsubstituted or substituted monovalent hydrocarbyl groups, for example, alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl; aryl groups such as phenyl, tolyl, xylyl, and naphthyl; and halogenated alkyl groups

15 such as 3-chloropropyl and 3,3,3-trifluoropropyl. Among these, methyl is the group most generally used because this facilitates industrial production, followed in terms of generality of use by the use of both methyl and phenyl. The viscosity of component (B) at 25°C is preferably 0.1 to 100,000 mPa·s, and more preferably 1 to 1,000 mPa·s.

[0021] Examples of component (B) include:

20 methylhydrogenpolysiloxanes endblocked by trimethylsiloxy at both terminals,

dimethylsiloxane-methylhydrogensiloxane copolymers endblocked by trimethylsiloxy at both terminals,

methylhydrogenpolysiloxanes endblocked by dimethylsiloxy at both terminals,

dimethylsiloxane-methylhydrogensiloxane copolymers endblocked by dimethylsiloxy at both

25 terminals,

cyclic methylhydrogensiloxane oligomers, and

tetrakis(dimethylhydrogensiloxy)silane.

Two or more types of component (B) can be used in combination.

[0022] Component (B) should be added in an amount sufficient to produce an elastomer
5 upon crosslinking with component (A) and should be present in an amount that provides a value of 0.1 to 10 for the molar ratio between the silicon-bonded hydrogen atoms in component (B) and the silicon-bonded alkenyl groups in component (A). Values of 0.3 to 0.8 are preferred when the cured product is to be a gel, while values of 0.8 to 5 are preferred when the cured product is to be a rubber. The content of component (B) per 100 weight
10 parts component (A) will vary as a function of the molecular weight of component (A) and the Si-bonded alkenyl content in component (A) and the molecular weight of component (B) and the Si-bonded hydrogen content in component (B). However, component (B) may be used at 0.1 to 50 weight parts per 100 weight parts component (A).

[0023] Component (C) is a catalyst that accelerates the hydrosilylation reaction between
15 the silicon-bonded alkenyl in component (A) and the silicon-bonded hydrogen in component (B). Component (C) can be exemplified by platinum catalysts, rhodium catalysts, and palladium catalysts, but viewed from the perspective of properties and ease of acquisition is preferably a platinum catalyst. The platinum catalysts can be exemplified by finely divided platinum powder, platinum black, platinum supported on finely divided silica powder,
20 platinum supported on active carbon, chloroplatinic acid, alcohol modifications of chloroplatinic acid, diolefin complexes of platinum, diketone complexes of platinum, dialkenyltetraalkyldisiloxane complexes of platinum, and finely divided thermoplastic resin powder containing a platinum catalyst as described above.

[0024] Component (C) is added in a catalytic quantity, that is, in an amount sufficient to
25 induce the hydrosilylation reaction of the silicon-bonded alkenyl in component (A) with the

silicon-bonded hydrogen in component (B). In the case of platinum catalysts, it will be sufficient to add component (C) in an amount that provides the composition with 0.1 to 1,000 weight-ppm platinum atoms in the composition. Two or more types of component (C) can be used in combination.

5 **[0025]** The hydrosilylation inhibitor (D) controls the rate of the hydrosilylation reaction between the Si-bonded alkenyl in component (A) and the Si-bonded hydrogen in component (B) in such a manner that curing is inhibited at ambient temperature while proceeding rapidly upon heating. Component (D) can be exemplified by alkyne alcohols such as 3-methyl-1-butyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, and phenylbutynol; ene-yne compounds such as 3-
10 methyl-3-penten-1-yne and 3,5-dimethyl-3-hexen-1-yne; as well as 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane, and benzotriazole. Component (D) will generally be added at from 0.01 to 5 weight parts per 100 weight parts component (A).

[0026] The thermoconductive silicone elastomer composition of this invention
15 comprising the thermoconductive filler (b) whose surface has been treated or coated with a fatty acid (a) and thereafter has also been treated or coated with an epoxy-functional compound (c) and a curing catalyst (d) and the aforementioned hydrosilylation-curing silicone elastomer composition contains preferably 9 to 98 weight %, more preferably 20 to 95 weight % the thermoconductive filler (b) whose surface has been treated or coated with a
20 fatty acid (a) and thereafter has also been treated or coated with an epoxy-functional compound (c) and a curing catalyst (d), as Component (E) . However, the appropriate addition of Component (E) should be selected as a function of the particular type of the thermoconductive filler so as to avoid an overly pronounced thickening or a loss of fluidity of the composition.

[0027] The thermoconductive silicone elastomer composition of this invention can contain one or more additives insofar as this does not impair the objects of this invention. These additives can be exemplified by reinforcing fillers (*e.g.*, fumed silica, wet-process silica), extender fillers, solvents, colorants, flame retardants, adhesion promoters, and non-reactive silicone oils. When a reinforcing filler is to be added, it is preferably mixed with the other components after it has been formulated as a silicone elastomer base by mixing with a cross-linkable diorganopolysiloxane such as component (A).

[0028] The adhesion promoter (F) is preferably an organosilane or organosiloxane oligomer that contains at least one silicon-bonded alkenyl groups or hydrogen atoms and at least two alkoxy groups bonded to the same silicon atom. The molecular structure of the organosiloxane oligomer can be exemplified by straight chain, partially branched straight chain, branched chain, and cyclic. The silicon-bonded alkenyl group in this component can be exemplified by vinyl, allyl, butenyl, pentenyl, and hexenyl with vinyl being preferred. The silicon-bonded alkoxy can be exemplified by methoxy, ethoxy, propoxy, butoxy, and methoxyethoxy with methoxy bonded to the same silicon atom being preferred. The silicon-bonded groups other than alkenyl and alkoxy can be exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl; aryl groups such as phenyl, tolyl, xylyl, and naphthyl; aralkyl groups such as benzyl and phenethyl; halogenated alkyl groups such as 3-chloropropyl and 3,3,3-trifluoropropyl; glycidoxyalkyl groups such as 3-glycidoxypropyl and 4-glycidoxybutyl; (3,4-epoxycyclohexyl)alkyl groups such as 2-(3,4-epoxycyclohexyl)ethyl and 3-(3,4-epoxycyclohexyl)propyl; and oxiranylalkyl groups such as 4-oxiranylbutyl and 8-oxiranyloctyl. The molecule preferably contains at least one epoxy-functional monovalent organic group since this can impart an excellent adhesiveness for a variety of substrates when the substrate is maintained in contact with the composition while the composition cures. This component can be specifically exemplified by

vinyltrimethoxysilane, allyltrimethoxysilane, hydrogentrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, the partial condensation product of 3-glycidoxypropyltrimethoxysilane and silanol-endblocked dimethylsiloxane oligomer, 3-methacryloxypropyltrimethoxysilane, and the partial condensation product of 3-methacryloxypropyltrimethoxysilane and silanol-endblocked dimethylsiloxane oligomer. The adhesion promoter is preferably fluid or liquid at ambient temperature and preferably has a viscosity at 25°C in the range of 1 to 500 mPa·s. This component is generally added at from 0.1 to 10 weight parts for each 100 weight parts component (A).

[0029] Viewed from the perspective of the processability at the point of use, the inventive thermoconductive silicone elastomer composition preferably is fluid or liquid at ambient temperature and preferably is heat-curing. The cured product may be a rubber or gel or a partially crosslinked, *i.e.*, semi-cured, elastomer or gel. The inventive thermoconductive silicone elastomer composition may also be electrically conductive.

[0030] The inventive thermoconductive silicone elastomer composition is useful as an adhesive, encapsulant, potting agent, or protective coating for electrical and electronic components and is extremely useful as an adhesive between a semiconductor chip and a heat-dissipating plate or heat sink. The inventive thermoconductive silicone elastomer composition will cure at room temperature when it is a hydrosilylation-curing silicone elastomer composition comprising the components (A) to (C) described above. However, when it is a hydrosilylation-curing silicone elastomer composition comprising the components (A) to (D) described above, it will undergo almost no cure at ambient temperature, but will cure rapidly upon heating. The heating temperature is preferably in the range from 50 to 250°C and more preferably is in the range of 80 to 200°C.

[0031] Semiconductor devices according to this invention comprise a semiconductor chip that is coated by cured product afforded by the aforementioned thermoconductive silicone elastomer composition. The semiconductor chip may be coated in whole or in part. The semiconductor chip can be bonded to another substrate, for example, a heat-dissipating plate or heat sink, by cured product afforded by the aforementioned thermoconductive silicone elastomer composition. The inventive semiconductor devices may comprise one or more semiconductor chips. The semiconductor chip can be exemplified by the semiconductor chips in diodes, transistors, thyristors, monolithic ICs, and hybrid ICs. The semiconductor device can be exemplified by diodes, transistors, thyristors, monolithic ICs, hybrid ICs, LSI, and VLSI.

[0032] Figure 1 contains a cross section of an LSI that is one example of a semiconductor device according to the present invention. A semiconductor chip **1** in the LSI in Figure 1 is mounted on a substrate for circuit **2**. The semiconductor chip **1** is electrically connected by gold bumps **4** to wirings **3** printed on the substrate for circuit **2**, while the wirings **3** are themselves connected to outer leads. A heat-dissipating plate **6** is mounted on the back side of the semiconductor chip **1**. A thermoconductive silicone rubber **5**, comprising the cured product of a thermoconductive silicone rubber composition, is present between the semiconductor chip **1** and the heat-dissipating plate **6**; this thermoconductive silicone rubber **5** adheres well to both the semiconductor chip **1** and the heat-dissipating plate **6**. The material of the substrate for circuit **2** can be, for example, an organic resin such as a polyimide resin, bismaleimide triazine resin, glass fiber-reinforced epoxy resin, Bakelite resin, or phenolic resin; a ceramic; or a metal such as copper or aluminum. The material of the wiring **3** can be exemplified by gold, copper, and silver-palladium. The gold bumps **4** can also be executed of a material other than gold, such as a gold alloy. The material of the heat-dissipating plate **6** can be exemplified by good heat

conducting metals such as aluminum, copper, and nickel. In addition to the semiconductor chip **1**, electronic components such as resistors, capacitors, coils, etc., can be mounted on the substrate for circuit **2**.

[0033] A semiconductor device according to this invention can be fabricated, for example, by mounting the semiconductor chip **1** on the substrate for circuit **2** and then electrically connecting this semiconductor chip **1** to the wirings **3** printed on the substrate for circuit **2** through the gold bumps **4**; thereafter coating the aforementioned thermoconductive silicone rubber composition **5** on the back side of the semiconductor chip **1**; setting the heat-dissipating plate **6** thereon; and heating at 50 to 200°C.

Examples

[0034] The thermoconductive filler, thermoconductive silicone rubber composition, and semiconductor devices according to this invention will be explained in detail through examples. The viscosity values reported in the examples were measured at 25°C. The thermal conductivity, hardness of the cured product, and semiconductor device reliability were measured for each thermoconductive silicone rubber composition as follows.

Measurement of the thermal conductivity of the thermoconductive silicone rubber

[0035] The thermoconductive silicone rubber composition was molded to dimensions of 15 centimeters (cm) × 6 cm with a thickness of 2 cm and was cured by heating for 1 hour in a convection oven at 150 °C. The thermal conductivity of the product was measured using a thermal conductivity measurement instrument (QTM-500 from Kyoto Denshi Co., Ltd.). The measurement was carried out through polyvinylidene chloride film (thickness = 10 μm) to prevent electrical leakage from the detector.

Measurement of the initial hardness of the thermoconductive silicone rubber

[0036] Using a durometer hardness tester in accordance with JIS K 6253, the hardness was measured on a thermoconductive silicone rubber sheet prepared by heating the thermoconductive silicone rubber composition for 1 hour in a convection oven at 150°C.

Measurement of the hardness of the thermoconductive silicone rubber after thermal ageing

[0037] The rubber sheet used for measurement of the initial hardness of the thermoconductive silicone rubber was heated for 24 hours in a convection oven at 150 °C and was then submitted to measurement of the hardness using the durometer hardness tester in accordance with JIS K 6253.

Evaluation of semiconductor device reliability

[0038] Twenty semiconductor devices as illustrated in Figure 1 were fabricated as follows. The semiconductor chip **1** was mounted on the substrate for circuit **2** (made of glass fiber-reinforced epoxy resin) having the wirings **3** printed on the surface of the substrate for circuit **2** and outer leads at the edge. The semiconductor chip **1** and the wirings **3** were then electrically connected by the gold bumps **4**. A thermoconductive silicone rubber composition was coated using a dispenser on the back side of the semiconductor chip **1** and a heat-dissipating plate **6** was applied thereon followed immediately by heating in a convection oven at 150 °C. This gave a semiconductor device in which the semiconductor chip **1** and heat-dissipating plate **6** were bonded to each other by the thermoconductive silicone rubber **5**.

[0039] Semiconductor devices fabricated as described above were subjected to 100 cycles of a thermal cycle test in which 1 cycle consisted of 30 minutes at –40°C and 30 minutes at +120°C. The thermoconductive silicone rubber **5** residing between the semiconductor chip **1** and the heat-dissipating plate **6** was then examined with a microscope for separation between it and the semiconductor chip **1** and for separation between it and the

aluminum heat-dissipating plate. Scoring the existence of separation as a defect, the number of such semiconductor devices (the defect rate) was determined.

Example 1

5 **[0040]** The following were mixed into 11.4 weight parts dimethylvinylsiloxy/trimethylsiloxy-terminated straight-chain dimethylpolysiloxane (component (A)) that had a viscosity of 600 mPa·s, a dimethylvinylsiloxy : trimethylsiloxy average molar ratio of 1 : 1, and a silicon-bonded vinyl content of 0.13 weight%: 85 weight parts reduced silver flake (component (b), average particle size = 10 μm, AgC-2190 from
10 Fukuda Metal Co., Ltd.) whose surface had been treated with oleic acid (component (a)), 1.0 weight part (3-glycidoxypropyl)dimethylsiloxy-endblocked dimethylsiloxane oligomer that had a viscosity of 25 mPa·s (component (c)), and 0.1 weight part aluminum trisacetylacetonate (component (d)). This mixture was heated for 1 hour at 90 °C to give reduced silver flake whose surface had been treated with oleic acid and thereafter also with
15 (3-glycidoxypropyl)dimethylsiloxy-endblocked dimethylsiloxane oligomer and aluminum trisacetylacetonate.

[0041] The following were mixed to homogeneity into this heat-treated mixture: 0.6 weight part trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer (component (B), viscosity = 20 mPa·s, silicon-bonded hydrogen content = 0.75
20 weight%), a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane/platinum complex (component (C), added in an amount that provided 5 weight-ppm platinum metal in the composition), and 0.01 weight part 3-phenyl-1-butyn-3-ol (component (D)). The product was a thermoconductive silicone rubber composition with a viscosity of 35 Pa·s.

[0042] The thermoconductive silicone rubber afforded by heating this thermoconductive silicone rubber composition for 1 hour at 150 °C was submitted to measurement of the thermal conductivity, initial hardness, hardness after thermal ageing, and semiconductor device reliability using the methods described above. The results of these evaluations are
5 reported in Table 1.

Comparative Example 1

[0043] A thermoconductive silicone rubber composition with a viscosity of 42 Pascal·seconds (Pa·s) was prepared according to the procedure of Example 1, but in this case
10 without using the 1.0 weight part (3-glycidoxypropyl)dimethylsiloxy-endblocked dimethylsiloxane oligomer that had a viscosity of 25 mPa·s (component (c)) and the 0.1 weight part aluminum tris(acetylacetonate) (component (d)).

[0044] The thermoconductive silicone rubber afforded by heating this thermoconductive silicone rubber composition for 1 hour at 150 °C was submitted to measurement of the
15 thermal conductivity, initial hardness, hardness after thermal ageing, and semiconductor device reliability using the methods described above. The results of these evaluations are reported in Table 1.

Example 2

20 [0045] The following were mixed into 11.4 weight parts dimethylvinylsiloxy-terminated dimethylpolysiloxane (component (A)) that had a viscosity of 400 mPa·s and a silicon-bonded vinyl content of 0.44 weight%: 85 weight parts reduced silver flake (component (b), average particle size = 10 μm, AgC-2190 from Fukuda Metal Co., Ltd.) whose surface had been treated with oleic acid (component (a)), 1.0 weight part branched polysiloxane with the

average formula $(RSiO_{3/2})_{0.18}(Me_2SiO_{2/2})_{0.47}(MeO_{1/2})_{0.35}$ (R = 3-glycidoxypropyl, Me = methyl) that had a viscosity of 20 mPa·s (component (c)), and 0.1 weight part aluminum tris(ethyl acetoacetate) (component (d)). This mixture was heated for 3 hours at 90 °C to give reduced silver flake whose surface had been treated with oleic acid and thereafter also
5 with the aforementioned branched polysiloxane and aluminum tris(ethyl acetoacetate).

[0046] The following were mixed to homogeneity into this heat-treated mixture: 0.03 weight part trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 20 mPa·s, silicon-bonded hydrogen content = 0.75 weight%) and 0.67 weight part dimethylhydrogensiloxy-endblocked dimethylpolysiloxane (viscosity = 15 mPa·s,
10 silicon-bonded hydrogen content = 0.12 weight%) as component (B), a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane/platinum complex (component (C), added in an amount that provided 5 weight-ppm platinum metal in the composition), and 0.01 weight part 3-phenyl-1-butyn-3-ol (component (D)). The product was a thermoconductive silicone rubber composition with a viscosity of 31 Pa·s.

15 **[0047]** The thermoconductive silicone rubber afforded by heating this thermoconductive silicone rubber composition for 1 hour at 150°C was submitted to measurement of the thermal conductivity, initial hardness, hardness after thermal ageing, and semiconductor device reliability using the methods described above. The results of these evaluations are reported in Table 1.

20

Comparative Example 2

[0048] A thermoconductive silicone rubber composition with a viscosity of 40 Pa·s was prepared according to the procedure of Example 2, but in this case without using the 1.0 weight part branched polysiloxane with the average formula

$(RSiO_{3/2})_{0.18}(Me_2SiO_{2/2})_{0.47}(MeO_{1/2})_{0.35}$ (R = 3-glycidoxypropyl, Me = methyl) that had a viscosity of 20 mPa·s (component (c)) and 0.1 weight part aluminum trisethyl acetoacetate (component (d)).

[0049] The thermoconductive silicone rubber afforded by heating this thermoconductive
5 silicone rubber composition for 1 hour at 150 °C was submitted to measurement of the thermal conductivity, initial hardness, hardness after thermal ageing, and semiconductor device reliability using the methods described above. The results of these evaluations are reported in Table 1.

10 Example 3

[0050] A thermoconductive silicone rubber composition with a viscosity of 55 Pa·s was prepared according to the procedure of Example 1, but in this case using 0.5 weight part bisphenol-type epoxy resin (epoxy value = 165, ZX-1059 from Toto Kasei Co., Ltd.) in place of the 1.0 weight part (3-glycidoxypropyl)dimethylsiloxy-endblocked dimethylsiloxane
15 oligomer that had a viscosity of 25 mPa·s (component (c)). The thermoconductive silicone rubber afforded by heating this thermoconductive silicone rubber composition for 1 hour at 150 °C was submitted to measurement of the thermal conductivity, initial hardness, hardness after thermal ageing, and semiconductor device reliability using the methods described above. The results of these evaluations are reported in Table 1.

20 Table 1.

Properties	Examples			Comparative examples	
	1	2	3	1	2
thermal conductivity of the thermo-conductive silicone rubber (W/m·K)	5.5	5.3	5.5	5.7	5.6
initial hardness of the thermoconductive silicone rubber	2	1	4	3	3

hardness of the thermoconductive silicone rubber after thermal ageing	4	3	9	*	*
evaluation of semiconductor device reliability, defect rate (%)	0	0	0	100	100

* = could not be measured due to embrittlement

Industrial Applicability

5 **[0051]** The thermoconductive filler according to this invention, which is characterized by its ability to impart thermal conductivity without impairing the thermal stability, is useful as a thickener or filler that can impart thermal conductivity to, curable silicone elastomer compositions, curable silicone resin compositions, silicone oil compounds, and so on. The thermoconductive silicone elastomer composition according to this invention, which is

10 characterized by the excellent thermal stability exhibited by its cured product, is useful as heat-dissipating adhesives, encapsulants, potting agents, and protective coatings for electrical and electronic components. The semiconductor device according to this invention, which is characterized by an excellent reliability, is useful for various electronic devices or apparatus.

15

CLAIMS

1. Thermoconductive filler whose surface has been treated or coated with a fatty acid and thereafter has also been treated or coated with an epoxy-functional compound and a curing
5 catalyst for epoxy resins.

2. The thermoconductive filler of claim 1, wherein the thermoconductive filler comprises a material selected from metal or a metal compound.

10 3. The thermoconductive filler of claim 2, wherein the fatty acid is higher fatty acid and the metal is silver.

4. Thermoconductive filler of any one of claims 1 to 3, wherein the epoxy-functional compound is an epoxy resin or epoxy-functional organopolysiloxane.

15

5. Thermoconductive silicone elastomer composition characterized by comprising the thermoconductive filler of claim 1 and a silicone elastomer composition.

6. The thermoconductive silicone elastomer composition of claim 5, wherein the fatty acid
20 is higher fatty acid and the material comprising the thermoconductive filler is silver.

7. The thermoconductive silicone elastomer composition of claim 5, wherein the silicone elastomer composition is a hydrosilylation-curing silicone elastomer composition.

8. The thermoconductive silicone elastomer composition of claim 7, wherein the hydrosilylation-curing silicone elastomer composition comprises

(A) a fluid organopolysiloxane that contains at least two silicon-bonded alkenyl groups in each molecule,

5 (B) a fluid organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule,

(C) a hydrosilylation catalyst, and optionally

(D) a hydrosilylation inhibitor.

10 9. The thermoconductive silicone elastomer composition described in claim 5, that contains 9 to 98 weight% of the thermoconductive filler.

10. A semiconductor device prepared by a method characterized by coating a semiconductor chip with a thermoconductive silicone elastomer composition as
15 described in any of claims 5 to 9 and curing.

11. The semiconductor device of claim 10, characterized in that the semiconductor chip is bonded to a heat-dissipating plate by the cured product of a thermoconductive silicone elastomer composition as described in any of claims 5 to 9.

20

Figure 1