# DESCRIPTION JP2012001604A

Siloxene composite material, siloxene derivative, and method for producing same

## [0001]

The present invention relates to a siloxene composite material, a siloxene derivative, and a method for producing the same.

## [0002]

Siloxene, represented by the formula Si<sub> 6 </sub>H<sub> a </sub>(OH)<sub> 6 − a </sub> (1≦a≦5), is a hydrogenated/hydroxide compound having a layered silicon skeleton, and has attracted attention as a light-emitting material or semiconductor material. However, because siloxene tends to aggregate, it is difficult to disperse it highly in a solution or resin or to form a uniform thin film, making it difficult to use it as is as a light-emitting or semiconducting material.

## [0003]

On the other hand, Z. Naturforsch., 1979, vol. 34b, pp. 25-30 (Non-Patent Document 1) discloses that a siloxene derivative in which an alkoxy group is bonded to the siloxene skeleton can be obtained by synthesizing siloxene in alcohol, and also shows that the interlayer distance of this alkoxylated siloxene derivative is larger than that of siloxene.
However, in the method described in Non-Patent Document 1, the functional groups that can be introduced into siloxene are limited to those contained in organic groups that do not inhibit siloxene synthesis and can be directly bonded to the siloxene skeleton, making it difficult to introduce any functional group into siloxene.

[0004]

38 Furthermore, Non-Patent Document 1 discloses that the interlayer distance can be adjusted by intercalating various amide compounds into the alkoxylated siloxane derivative.

41 However, in the method described in Non-Patent Document 1, the organic groups that can be bonded to the siloxene skeleton are limited, making it difficult to insert any intercalant between the layers.

[0005]

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[0006]

51 The present invention has been made in consideration of the problems associated with the above-mentioned conventional techniques, and has an object to provide a method for producing a siloxene composite material in which the functional group to be introduced into siloxene can be selected arbitrarily, a siloxene composite material obtained thereby, and a siloxene derivative to be used in the production method and a method for producing the same.

[0007]

59 As a result of intensive research conducted by the inventors in order to achieve the above-mentioned object, they discovered that by reacting a metal silicide with a hydroxycarboxylic acid ester in the presence of an acid, a siloxene derivative in which an organic group having a carboxylic acid ester group is bonded to the siloxene skeleton can be obtained, and further, by reacting this siloxene derivative with an amine compound having an arbitrary functional group or an arbitrary nitrogen-containing aromatic heterocyclic compound, it is possible to introduce an arbitrary functional group into the siloxene, thereby completing the present invention.

[0008]

70 That is, the siloxene composite material of the present invention has the following composition formula (1): Si<sub> 6 </sub>H<sub> a </sub>(O-E-CONR<sup> 1 </sup>R<sup> 2 </sup>)<sub> 6 − a </sub> (1) (In formula (1), R<sup> 1 </sup> and R<sup> 2 </sup> each independently represent a hydrogen atom, or a hydrocarbon group or hetero group which may have a substituent, and in the NR<sup> 1 </sup>R<sup> 2 </sup>, R<sup> 1 </sup> and R<sup> 2 </sup> may be bonded to each other to form a nitrogen-containing heterocycle, E represents a hydrocarbon group having 1 to 30 carbon atoms, and 1≦a≦5.

78 ) is characterized in that it is represented by the formula:

## [0009]

The siloxene derivative of the present invention has the following composition formula (2): SiNERHNER(O-E-COORNER)NER (2) (wherein RNER represents a hydrocarbon group having 1 to 10 carbon atoms, E represents a hydrocarbon group having 1 to 30 carbon atoms, and 1≦a≦5.

) is characterized in that it is represented by the formula:

## [0010]

Furthermore, the present invention provides a method for producing a siloxene composite material comprising the steps of:

) and a siloxane derivative represented by the following formula (3): HNR<sup> 1 </sup>R<sup> 2 </sup> (3) (In formula (3), R<sup> 1 </sup> and R<sup> 2 </sup> each independently represent a hydrogen atom, or a hydrocarbon group or hetero group which may have a substituent, and in the NR<sup> 1 </sup>R<sup> 2 </sup>, R<sup> 1 </sup> and R<sup> 2 </sup> may be bonded to each other to form a nitrogen-containing heterocycle.

) in an organic solvent to obtain a compound represented by the following composition formula (1): Si<sub> 6 </sub>H<sub> a </sub>(O-E-CONR<sup> 1 </sup>R<sup> 2 </sup>)<sub> 6 − a </sub> (1) (In formula (1), R<sup> 1 </sup> and R<sup> 2 </sup> are the same as R<sup> 1 </sup> and R<sup> 2 </sup> in formula (3), and E and a are the same as E and a in formula (2).

The present invention is characterized in that a siloxene composite material represented by the formula:

## [0011]

The method for producing a siloxene derivative of the present invention comprises the steps of: (M) NER (Si) NER (4) (in formula (4), M is at least one metal atom selected from the group consisting of alkali metals, alkaline earth metals, terbium and thorium, x is an integer of 1 to 12, y is an integer of 1 to 17, and x≦y).

) and a metal silicide represented by the following formula (5): HO-E-COOR NER44 (5) (In formula (5), R NER45 represents a hydrocarbon group having 1 to 10 carbon atoms, and E represents a hydrocarbon group having 1 to 30 carbon atoms.

) in the presence of an acid to obtain a hydroxycarboxylic acid ester represented by the following composition formula (2): SiNER46HNER47(O-E-COORNER48)NER49 (2) (In formula (2), RNER50 and E are the same as RNER51 and E in formula (5), and 1≦a≦5.

The present invention is characterized in that a siloxane derivative represented by the formula:

## [0012]

*123* According to the present invention, it is possible to obtain a siloxene derivative in which an organic group having a carboxylate group is bonded to a siloxene skeleton.

*123* Furthermore, by using this siloxene derivative, it becomes possible to introduce any functional group into the siloxene.

## [0013]

*130* FIG. 1 is a schematic diagram showing the chemical structure of a siloxene derivative of the present invention.

*132* FIG. 1 is a schematic diagram showing the chemical structure of a siloxene composite material of the present invention.

*134* 1 is a graph showing an infrared absorption spectrum of the siloxene derivative obtained in Example 1.

*136* 1 is a graph showing the X-ray diffraction pattern of the siloxene derivative obtained in Example 1.

*138* 1 is a graph showing an infrared absorption spectrum of the siloxene composite material obtained in Example 2.

*140* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 2.

*142* 1 is a graph showing an infrared absorption spectrum of the siloxene composite material obtained in Example 3.

*144* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 3.

*146* 1 is a graph showing an infrared absorption spectrum of the siloxene composite material obtained in Example 4.

*148* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 4.

*150* 1 is a graph showing an infrared absorption spectrum of the siloxene composite material obtained in Example 5.

*152* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 5.

*154* 1 is a graph showing an infrared absorption spectrum of the siloxene composite material obtained in Example 6.

*156* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 6.

*158* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 7.

*160* 1 is a graph showing the X-ray diffraction pattern of the siloxene composite material obtained in Example 8.

*162* 1 is a graph showing the fluorescence spectra of the siloxene composite material obtained in Example 8 and the siloxene derivative obtained in Comparative Example 1.

*164* 1 is a graph showing the excitation spectra of the siloxene composite material obtained in

Example 8 and the siloxene derivative obtained in Comparative Example 1.

[0014]

The present invention will be described in detail below based on preferred embodiments thereof.

[0015]

First, the siloxene derivative of the present invention and the method for producing the same will be described.

[0016]

<Siloxene Derivative> The siloxene derivative of the present invention has the following composition formula (2): SiNER52HNER53(O-E-COORNER54)NER55(2) (In formula (2), RNER56 represents a hydrocarbon group having 1 to 10 carbon atoms, E represents a hydrocarbon group having 1 to 30 carbon atoms, and 1≦a≦5.

) is expressed as follows.

[0017]

Furthermore, when a structure formed by six silicon atoms of the siloxene skeleton is regarded as one constituent unit, the primary structure of the siloxene derivative of the present invention is represented by the following formula (2a): [Si<sub> 6 </sub>H<sub> n </sub>(O-E-COOR<sup> 3 </sup>)<sub> 6－n </sub>]<sub>m</sub> (2a) (In formula (2a), R<sup> 3 </sup> and E are defined as R<sup> 3 </sup> and E in formula (2), n is independently an integer of 1 to 5 for each constituent unit, and m is not particularly limited and is, for example, an integer of 500 to 600,000,000.

) is expressed as follows.

[0018]

The shape of such a siloxene derivative is not particularly limited, but from the viewpoints of ease of controlling the film thickness when forming a film of the siloxene derivative and ease of control of the morphology of the reaction product (e.g., the siloxene composite material of the present invention), a layer or sheet shape is preferred.

FIG. 1 shows an example of the siloxene derivative of the present invention being a layered compound, but the structure of the siloxene derivative of the present invention is not limited to this.

[0019]

211 In the siloxene derivative of the present invention, it is usually preferred that the silicon atoms are bonded to each other to form a substantially planar shape.
213 The siloxene skeleton formed by the silicon atoms is preferably a skeleton corresponding to the Si(111) surface of single crystal silicon.
215 Furthermore, it is preferable that the organic group having a carboxylate group (-O-E-COOR<sup> 3 </sup>) is arranged in a direction perpendicular to the approximate plane formed by the silicon atoms.

[0020]

221 In the siloxene derivative of the present invention, the hydrocarbon group constituting R<sup> 3 </sup> in the formula (2), the formula (2a) and FIG. 1 is a monovalent hydrocarbon group having 1 to 10 carbon atoms.
224 If the number of carbon atoms in the hydrocarbon group constituting R<sup> 3 </sup> exceeds the upper limit, R<sup> 3 </sup> will be difficult to eliminate when producing the siloxene composite material of the present invention described below, the reactivity of the carboxylic acid ester group with the amino group will decrease, and an amide bond will not be formed, making it difficult to obtain the siloxene composite material of the present invention.
230 Therefore, from the viewpoint of ease of elimination of R<sup> 3 </sup>, the number of carbon atoms in the hydrocarbon group constituting R<sup> 3 </sup> is preferably 1 to 5, and more preferably 1 to 3.

[0021]

236 The hydrocarbon group constituting R<sup> 3 </sup> may be linear, branched, or cyclic, but a linear hydrocarbon group is preferred as R<sup> 3 </sup> from the viewpoint that the bulkiness of R<sup> 3 </sup> is less likely to inhibit the amidation reaction in the reaction between the carboxylic acid ester group and the amino group.
240 In addition, two or more kinds of hydrocarbon groups may be present as R<sup> 3 </sup> in one molecule of the siloxene derivative.
242 Furthermore, when a plurality of R<sup> 3 </sup> are present in one structural unit (when n in the above formula (2a) is 1 to 4), they may be the same or different from each other.

[0022]

247 Examples of the hydrocarbon groups constituting R<sup> 3 </sup> include linear, branched or cyclic saturated hydrocarbon groups such as methyl, ethyl, propyl, butyl, and hexyl groups; linear, branched or cyclic unsaturated hydrocarbon groups such as vinyl, allyl, butenyl, and hexenyl groups; and aromatic hydrocarbon groups such as phenyl, benzyl, and tolyl groups.

Of these hydrocarbon groups, from the viewpoint that R<sup> 3 </sup> is less likely to inhibit the amidation reaction in the reaction between the carboxylate group and the amino group, linear saturated hydrocarbon groups and linear unsaturated hydrocarbon groups are preferred, with methyl groups and ethyl groups being particularly preferred.

[0023]

In the siloxene derivative of the present invention, the hydrocarbon group constituting E in the formula (2), the formula (2a) and FIG. 1 is a divalent hydrocarbon group having 1 to 30 carbon atoms.
When the siloxene derivative of the present invention is a layered compound, the interlayer distance of the siloxene derivative or the siloxene composite material of the present invention obtained therefrom can be controlled by adjusting the number of carbon atoms in the hydrocarbon group constituting this E.
On the other hand, when the number of carbon atoms in the hydrocarbon group constituting E exceeds the upper limit, the organic group having a carboxylate group (-O-E-COOR<sup> 3 </sup>) becomes bulky, making it difficult to introduce the organic group having a carboxylate group between the layers of the siloxene derivative.
In particular, when an organic group having a carboxylate group is introduced using a hydroxycarboxylate ester described below, it becomes difficult for the hydroxycarboxylate to penetrate between the layers of the siloxene skeleton, making it difficult to bond the organic group having a carboxylate group (-O-E-COOR<sup> 3 </sup>) to the siloxene skeleton.
Therefore, from the viewpoint of facilitating the introduction of an organic group having a carboxylate group between layers of the siloxene derivative, the hydrocarbon group constituting E preferably has 1 to 15 carbon atoms, more preferably 1 to 10 carbon atoms, and particularly preferably 1 to 5 carbon atoms.

[0024]

The hydrocarbon group constituting E may be linear, branched, or cyclic. However, a linear hydrocarbon group is preferred from the viewpoints that the bulkiness of E is less likely to inhibit the amidation reaction in the reaction between the carboxylate group and the amino group during the production of the siloxene composite material of the present invention described below, and that the reactivity of the carboxylate group is less likely to decrease.

[0025]

Examples of the hydrocarbon group constituting E include linear, branched or cyclic saturated hydrocarbon groups such as a methylene group, an ethylene group, a propylene group, a butylene group, a hexylene group, an octylene group, or a decylene group; linear, branched or cyclic unsaturated hydrocarbon groups such as a vinylene group, an allylene group, a butenylene group, or a hexenylene group; and aromatic hydrocarbon groups such as a

phenylene group, a benzylene group, or a tolylene group.
298 Of these hydrocarbon groups, from the viewpoint that the hydrocarbon group constituting E is unlikely to change the properties attributable to the siloxene skeleton, a hydrocarbon group having as short a carbon chain as possible (for example, a hydrocarbon group having 1 to 5 carbon atoms) is preferred, and a methylene group or an ethylene group is particularly preferred.

[0026]

307 The siloxene derivative of the present invention has an easily detachable hydrocarbon group (R<sup> 3 </sup> in the above formula (2), the above formula (2a) and in FIG. 1) in the organic group bonded to the siloxene skeleton, and therefore the reaction between the carboxylate group and the amino group described below proceeds easily, making it possible to easily produce the siloxene composite material of the present invention.
312 Furthermore, when the siloxene derivative of the present invention is a layered compound as shown in FIG. 1 , the interlayer distance can be appropriately controlled by adjusting the number of carbon atoms in the organic group bonded to the siloxene skeleton. This makes it easier for a nitrogen-containing compound to enter between the layers of the siloxene derivative in the method for producing a siloxene composite material of the present invention described below, and makes it possible to easily react the carboxylate groups between the layers of the siloxene derivative with the amino groups of the nitrogen-containing compound.

[0027]

323 <Method for Producing Siloxene Derivative> The siloxene derivative of the present invention can be produced by reacting a metal silicide with a hydroxycarboxylic acid ester in the presence of an acid.

[0028]

329 The metal silicide used in the method for producing a siloxene derivative of the present invention is represented by the following formula (4): (M) NER (Si) NER (4) (In formula (4), M is at least one metal atom selected from the group consisting of alkali metals, alkaline earth metals, terbium and thorium, x is an integer of 1 to 12, y is an integer of 1 to 17, and $x \leqq y$.
333 It should be noted that x and y are determined depending on the type of the metal atom M.
334 ) is expressed as follows.

[0029]

338 In the formula (4), M is at least one metal atom selected from the group consisting of alkali metals (lithium, sodium, etc.), alkaline earth metals (calcium, strontium, barium, etc.),

terbium, and thorium. Of these metal atoms, calcium and strontium are preferred from the viewpoint that the silicon skeleton of the siloxene derivative forms a network within the crystal.

[0030]

Specific examples of the metal silicide include monocalcium disilicide, monocalcium monosilicide, and strontium disilicide. Among these, monocalcium disilicide is particularly preferred from the viewpoint of obtaining layered or sheet-like siloxene derivatives and siloxene composite materials.

[0031]

The hydroxycarboxylic acid ester used in the method for producing a siloxene derivative of the present invention is represented by the following formula (5): HO-E-COOR NER (5) (In formula (5), R NER and E are the same as R NER and E in formula (2) above. ) is expressed as follows.

[0032]

Such hydroxycarboxylic acids include glycolic acid alkyl esters (for example, methyl glycolate), hydroxybenzoic acid alkyl esters (for example, methyl p-hydroxybenzoate), and the like. Among these, from the viewpoint of enabling precise control of the interlayer distance of the siloxene derivative or the siloxene composite material obtained therefrom, alkyl glycolate is preferred, and methyl glycolate is particularly preferred.

[0033]

In the method for producing a siloxene derivative of the present invention, such a metal silicide is reacted with a hydroxycarboxylic acid ester in the presence of an acid to produce a siloxene derivative represented by the formula (2) or (2a) in which an organic group having a carboxylic acid ester group (-O-E-COOR<sup> 3 </sup>) is bonded to the siloxene skeleton. In the siloxene derivative thus formed, R<sup> 3 </sup> and E in the formula (2) and the formula (2a) are the same as R<sup> 3 </sup> and E in the formula (5). The mixing ratio of the metal silicide and the hydroxycarboxylic acid ester in the above reaction is not particularly limited, but it is preferable that the amount of the hydroxycarboxylic acid ester is at least 1 mole per mole of the metal silicide.

[0034]

The acid used in the above reaction includes hydrogen chloride, tetrafluoroboric acid, and the like.

The source of such an acid is not particularly limited, and examples of sources of hydrogen chloride include hydrogen chloride gas, concentrated hydrochloric acid, and hydrogen chloride-containing organic solvents.

Examples of the supply method include a method of bubbling hydrogen chloride gas into a hydroxycarboxylate ester, a method of adding concentrated hydrochloric acid to a hydroxycarboxylate ester, and a method of mixing a hydroxycarboxylate ester with an organic solvent containing hydrogen chloride. Among these, the method of bubbling hydrogen chloride gas into a hydroxycarboxylate ester is preferred.

There is no particular lower limit to the concentration of the acid, but it is preferable that the amount of the acid is 10 moles or more per mole of the metal silicide.

There is no particular upper limit to the acid concentration, but it is preferably 20 mol or less per mol of metal silicide.

## [0035]

In the method for producing a siloxene derivative of the present invention, a solvent may be used as necessary.

As such a solvent, an organic solvent other than alcohol is preferable, and 1,4-dioxane is more preferable.

It is particularly preferable to use, as the solvent, an organic solvent that has been subjected to a dehydration treatment.

In the reaction between a metal silicide and a hydroxycarboxylic acid ester, the presence of water or alcohol tends to produce siloxene having a hydroxyl group bonded to the siloxene skeleton or a siloxene derivative having an alkoxyl group bonded to the siloxene skeleton, and the yield of the siloxene derivative of the present invention tends to decrease.

The amount of the solvent used is not particularly limited, but it is preferable to use an amount that results in a metal silicide concentration of 1 to 10 mol/L.

## [0036]

In the reaction of the metal silicide with the hydroxycarboxylic acid ester according to the present invention, the reaction temperature is preferably 40 to 70 ° C., and the reaction time is preferably 10 to 20 hours.

The reaction between the metal silicide and the hydroxycarboxylic acid ester is preferably carried out in an atmosphere of an inert gas such as argon gas or nitrogen gas.

## [0037]

Next, the siloxene composite material of the present invention and the method for producing the same will be described.

[0038]

<Siloxene Composite Material> The siloxene composite material of the present invention has the following composition formula (1): Si<sub>６</sub>H<sub>ａ</sub>(O-E-CONR<sup>１</sup>R<sup>２</sup>)<sub>６－ａ</sub> (1) (In formula (1), R<sup>１</sup> and R<sup>２</sup> each independently represent a hydrogen atom, or a hydrocarbon group or hetero group which may have a substituent, and in the NR<sup>１</sup>R<sup>２</sup>, R<sup>１</sup> and R<sup>２</sup> may be bonded to each other to form a nitrogen-containing heterocycle, E represents a hydrocarbon group having 1 to 30 carbon atoms, and １≦a≦５.

) is expressed as follows.

[0039]

Furthermore, when a structure formed by six silicon atoms of a siloxene skeleton is regarded as one constituent unit, the primary structure of the siloxene composite material of the present invention is represented by the following formula (1a): [Si<sub>６</sub>H<sub>ｎ</sub>(O-E-CONR<sup>１</sup>R<sup>２</sup>)<sub>６－ｎ</sub>]<sub>ｍ</sub> (1a) (In formula (1a), R<sup>１</sup>, R<sup>２</sup> and E are defined as R<sup>１</sup>, R<sup>２</sup> and E in formula (1), n is independently an integer of 1 to 5 for each constituent unit, and m is not particularly limited and is, for example, an integer of 500 to 600,000,000.

) is expressed as follows.

[0040]

The shape of the siloxene composite material of the present invention is not particularly limited, but from the viewpoint of regularly arranging a layer (inorganic layer) made of a siloxene skeleton and a layer (organic layer) made of an organic group having an amide bond (O-E-CONR<sup>１</sup>R<sup>２</sup>), it is preferably in the form of a layer or sheet.

FIG. 2 shows an example of the siloxene composite material of the present invention in the form of a layered compound, but the structure of the siloxene composite material of the present invention is not limited to this.

[0041]

In the siloxene composite material of the present invention, it is generally preferred that the silicon atoms be bonded together to form a generally planar shape.

The siloxene skeleton formed by the silicon atoms is preferably a skeleton corresponding to the Si(111) surface of single crystal silicon.

Furthermore, the organic group having an amide bond (-OE-

CONR<sup> 1 </sup>R<sup> 2 </sup>) is preferably arranged in a direction perpendicular to the approximate plane formed by the silicon atoms.

[0042]

In the siloxene composite material of the present invention, in the formula (1), in the formula (1a) and in FIG. 2, R<sup> 1 </sup> and R<sup> 2 </sup> each independently represent a hydrogen atom, or a hydrocarbon group or a hetero group which may have a substituent. At least one of R<sup> 1 </sup> and R<sup> 2 </sup> is preferably a hydrocarbon group or a hetero group which may have a substituent.

[0043]

The number of carbon atoms in the hydrocarbon group and hetero group constituting R<sup> 1 </sup> and R<sup> 2 </sup> is not particularly limited, but is preferably 1 to 30, more preferably 1 to 15, and particularly preferably 1 to 10. The number of carbon atoms includes the number of carbon atoms of the substituents which may be bonded to the hydrocarbon group and the hetero group. When the siloxene composite material of the present invention is a layered compound, the interlayer distance of the siloxene composite material can be controlled by adjusting the carbon numbers of the hydrocarbon groups and hetero groups that constitute R<sup> 1 </sup> and R<sup> 2 </sup>. On the other hand, when the number of carbon atoms in the hydrocarbon groups and hetero groups constituting R<sup> 1 </sup> and R<sup> 2 </sup> exceeds the upper limit, the organic group having an amide bond (-O-E-CONR<sup> 1 </sup>R<sup> 2 </sup>) becomes bulky, and it tends to become difficult to introduce the organic group having an amide bond between the layers of the siloxene composite material. In particular, when an organic group having an amide bond is introduced by a reaction with a nitrogen-containing compound described below, it tends to be difficult for the nitrogen-containing compound to penetrate between the layers of the siloxene derivative, making it difficult to react the carboxylic acid ester group with the amino group of the nitrogen-containing compound between the layers of the siloxene derivative.

[0044]

In addition, the hydrocarbon groups and hetero groups constituting R<sup> 1 </sup> and R<sup> 2 </sup> may be linear, branched, or cyclic, but from the viewpoint of improving the optical properties and semiconductor characteristics of the siloxene composite material, cyclic unsaturated hydrocarbon groups and cyclic hetero groups are preferred.

[0045]

513 Examples of the hydrocarbon groups constituting R<sup> 1 </sup> and R<sup> 2 </sup> include linear, branched or cyclic saturated hydrocarbon groups such as methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, and dodecyl groups; linear, branched or cyclic unsaturated hydrocarbon groups such as vinyl, allyl, butenyl, and hexenyl groups; and aromatic hydrocarbon groups such as phenyl, benzyl, and tolyl groups.

513 Examples of the hetero group constituting R<sup> 1 </sup> and R<sup> 2 </sup> include nitrogen-containing aromatic heterocycles such as a pyrrole ring, an imidazole ring, and a pyridine ring, and an amino group.

[0046]

524 Substituents which may be bonded to the hydrocarbon groups and hetero groups constituting R<sup> 1 </sup> and R<sup> 2 </sup> include nitrogen-containing aromatic heterocycles such as a pyrrole ring, an imidazole ring, and a pyridine ring; sulfur-containing aromatic heterocycles such as a thiophene ring; and an amino group.

528 In particular, when the hydrocarbon group and the hetero group have an amino group as a substituent, they tend to form an amide bond with the carboxylic acid ester group of the adjacent siloxene skeleton, and a siloxene composite material in which adjacent siloxene skeletons are crosslinked with each other can be obtained.

[0047]

535 In the siloxene composite material of the present invention, R<sup> 1 </sup> and R<sup> 2 </sup> in the formula (1), the formula (1a) and FIG. 2 may be bonded to each other to form a nitrogen-containing heterocycle.

538 Examples of such a nitrogen-containing heterocycle include a pyrrole ring, an imidazole ring, and a pyridine ring.

540 In addition, such a nitrogen-containing heterocycle may have the above-mentioned substituents bonded thereto.

[0048]

545 The types of such hydrocarbon groups, hetero groups, substituents, and nitrogen-containing heterocycles can be appropriately selected depending on the desired properties to be imparted to the siloxene.

[0049]

551 In the siloxene composite material of the present invention, the hydrocarbon group constituting E in formula (1), formula (1a) and FIG. 2 is a divalent hydrocarbon group having 1 to 30 carbon atoms.

554 When the siloxene composite material of the present invention is a layered compound, the

interlayer distance of the siloxene composite material can be controlled by adjusting the number of carbon atoms in the hydrocarbon group constituting this E.

*556* On the other hand, if the number of carbon atoms in the hydrocarbon group constituting E exceeds the upper limit, the organic group having an amide bond (-O-E-CONR<sup> 1 </sup>R<sup> 2 </sup>) becomes bulky, making it difficult to introduce an organic group having an amide bond between the layers of the siloxene composite material.

*562* In particular, when a siloxene composite material is produced using the siloxene derivative of the present invention, it is difficult to obtain the siloxene derivative itself.

*564* Therefore, from the viewpoint of facilitating the introduction of an organic group having an amide bond between layers of the siloxene composite material, the hydrocarbon group constituting E preferably has 1 to 15 carbon atoms, more preferably 1 to 10 carbon atoms, and particularly preferably 1 to 5 carbon atoms.

## [0050]

*571* In addition, the hydrocarbon group constituting E may be linear, branched, or cyclic. However, from the viewpoints that the bulkiness of E is unlikely to inhibit the amidation reaction in the reaction between the carboxylate group and the amino group, and that the reactivity of the carboxylate group is unlikely to decrease, a linear hydrocarbon group is preferred.

## [0051]

*579* Examples of the hydrocarbon group constituting E include the hydrocarbon groups exemplified in the siloxene derivative of the present invention, and among them, a hydrocarbon group having as short a carbon chain as possible (e.g., a hydrocarbon group having 1 to 5 carbon atoms) that is unlikely to affect the properties resulting from the siloxene skeleton and the hydrocarbon groups and hetero groups constituting R<sup> 1 </sup> and R<sup> 2 </sup> is preferred, with a methylene group and an ethylene group being particularly preferred.

## [0052]

*589* Since the siloxene composite material of the present invention has an amide bond in the organic group bonded to the siloxene skeleton, the absorptivity of light in the ultraviolet region (particularly the region with a wavelength of 260 to 300 nm) tends to be higher than in the case where an organic group not having an amide bond is introduced.

*593* In addition, since the siloxene skeleton which is the basic skeleton thereof corresponds to silicon (particularly preferably, to the Si(111) surface of single crystal silicon), it tends to exhibit properties similar to those of silicon.

*596* For example, the fluorescence spectrum exhibited is similar to that of layered polysilane or siloxene having a skeleton corresponding to the similar Si(111) surface.

*598* In particular, the fluorescence spectrum is similar to that of layered polysilanes and siloxenes even when the excitation wavelength is in the ultraviolet region.

## [0053]

*603* Furthermore, when the siloxene composite material of the present invention is a layered compound as shown in FIG. 2, the interlayer distance varies depending on the number of carbon atoms in the organic group bonded to the siloxene skeleton.

## [0054]

*609* <Method of Producing Siloxene Composite Material> The siloxene composite material of the present invention can be produced by reacting the siloxene derivative of the present invention with a nitrogen-containing compound having an NH group in an organic solvent.

## [0055]

*615* The nitrogen-containing compound used in the method for producing a siloxene composite material of the present invention is represented by the following formula (3): HNR NER139 R NER140 (3) (In formula (3), R NER141 and R NER142 have the same meanings as R NER143 and R NER144 in formula (1) above.
*619* ) is expressed as follows.

## [0056]

*623* Examples of such nitrogen-containing compounds include unsubstituted amine compounds such as alkylamines (e.g., decylamine); substituted amine compounds such as aminoalkylimidazoles (e.g., aminopropylimidazole), aminoalkylthiophenes (e.g., aminoethylthiophene), and diaminoalkanes (e.g., diaminododecane); heterocycle-containing amine compounds such as aminopyrrole, aminoimidazole, and aminopyridine; and nitrogen-containing aromatic heterocyclic compounds such as imidazole, pyrrole, and pyridine.

## [0057]

*632* In the method for producing a siloxene composite material of the present invention, the siloxene derivative of the present invention is reacted with such a nitrogen-containing compound in an organic solvent to produce a siloxene composite material represented by formula (1) and formula (1a) in which an organic group having an amide bond (-O-E-CONR<sup> **1** </sup>R<sup> **2** </sup>) is bonded to the siloxene skeleton.
*637* The amide bond is represented by the following reaction formula (6):

[0059]

As shown in Figure 1, the nitrogen-containing compound is produced by selectively reacting with the carboxylic acid ester group of the siloxene derivative compared to the SiH group. In the siloxene composite material thus produced, R<sup> 1 </sup> and R<sup> 2 </sup> in the formula (1) and the formula (1a) are the same as R<sup> 1 </sup> and R<sup> 2 </sup> in the formula (3), E in the formula (1) and the formula (1a) is the same as E in the formula (2) and the formula (2a), a in the formula (1) is the same as a in the formula (2), and m and n in the formula (1a) are the same as m and n in the formula (2a). The mixing ratio of the siloxene derivative and the nitrogen-containing compound in the above reaction is not particularly limited, but it is preferable that the number of NH groups of the nitrogen-containing compound is 1 mole or more (more preferably 1 to 10 moles) per mole of carboxylate groups in the siloxene derivative.

[0060]

In the reaction between the siloxene derivative and the nitrogen-containing compound, it is preferable to use a solvent as necessary. As such a solvent, organic solvents other than alcohols are preferred, and acetonitrile and pyridine are more preferred. It is particularly preferable to use, as the solvent, an organic solvent that has been subjected to a dehydration treatment. In the reaction between a siloxene derivative and a nitrogen-containing compound, if water or alcohol is present, the hydrogen atoms bonded to the silicon atoms in the siloxene skeleton tend to be replaced by hydroxyl groups or alkoxy groups. The amount of the solvent used is not particularly limited, but it is preferable to use an amount that results in a siloxene derivative concentration of 0.1 to 10 mol/L.

[0061]

In the reaction of the siloxene derivative with the nitrogen-containing compound according to the present invention, the reaction temperature is preferably 40 to 100 ° C., more preferably 60 to 80 ° C., and the reaction time is preferably 10 to 100 hours. The reaction between the siloxene derivative and the nitrogen-containing compound is preferably carried out in an atmosphere of an inert gas such as argon gas or nitrogen gas.

[0062]

In the method for producing a siloxene composite material of the present invention, the NH group of the nitrogen-containing compound is reacted with the carboxylate group of the siloxene derivative of the present invention, so by using a compound having a desired functional group as the nitrogen-containing compound, it becomes possible to introduce the desired functional group into the siloxene composite material.

*682* This makes it possible to change or control the properties of siloxene (for example, optical properties and semiconductor properties).
*682* It will also be possible to impart new properties to siloxene composite materials.
*685* Furthermore, when guest molecules or guest ions are intercalated between the layers of a siloxene composite material, the affinity with the guest molecules or guest ions can be adjusted by changing the type of functional group introduced into the siloxene composite material, making it possible to control the intercalation.

[0063]

*692* Furthermore, when the siloxene composite material is a layered compound as shown in FIG. 2, in the method for producing a siloxene composite material of the present invention, it is possible to freely control the interlayer distance of the siloxene composite material by the type of nitrogen-containing compound used (in particular, the number of carbon atoms in the hydrocarbon group and hetero group constituting $R^1$ and $R^2$ in formula (3)).
*698* As a result, even when guest molecules or guest ions are intercalated between the layers of the siloxene composite material, it is possible for the guest molecules or guest ions to easily enter and exit the spaces between the layers without drastically changing the shape of the siloxene composite material.

[0064]

*705* The present invention will be described in more detail below based on examples and comparative examples, but the present invention is not limited to the following examples.

[0065]

*710* Example 1 Sulfuric acid (6 ml) was added to ammonium chloride (20 g) to generate hydrogen chloride gas, and this hydrogen chloride gas was bubbled into methyl glycolate (25 g) to prepare a hydrogen chloride-containing methyl glycolate solution.
*713* Calcium disilicide ($CaSi_2$, 244.3 mg) was placed in a Schlenk flask and purged with argon gas using a vacuum line.
*715* The hydrogen chloride-containing methyl glycolate solution (10 ml, approximately 50 moles of methyl glycolate per mole of calcium disilicide) was added to this Schlenk flask at room temperature, and then the mixture was heated and stirred at 60 ° C. for 15 hours to react calcium disilicide with methyl glycolate in the presence of hydrogen chloride under an argon atmosphere.

[0066]

*723* After the reaction was completed, hydrogen chloride was removed from the solution at room temperature under reduced pressure, and then dehydrated N,N-dimethylformamide (DMF, 5 ml) was added to prepare a suspension.

*725* This suspension was filtered under reduced pressure using a Teflon (registered trademark) filter having a pore size of 10 μm.

*729* The filter cake was washed three times with anhydrous acetone (5 ml each time) and then vacuum dried at 25 ° C. for 1 hour to obtain a pale yellow powder (290.8 mg).

[0067]

*734* The infrared absorption spectrum and the X-ray diffraction pattern of the resulting pale yellow powder are shown in FIG. 3 and FIG. 4, respectively.

*736* In the infrared absorption spectrum shown in FIG. 3, peaks derived from the Si—H bond and Si—O bond of the siloxene skeleton, as well as a peak derived from the carbonyl group of methyl glycolate bonded to the siloxene skeleton, were observed. The obtained pale yellow powder had a composition represented by the following formula (7): Si<sub> 6 </sub>H<sub> a </sub>(O—CH<sub> 2 </sub>-COOCH<sub> 3 </sub>)<sub> 6 − a </sub> (7) (in formula (7), 1≦a≦5).

*742* ) and the following structural formula (7a): [Si NER159 H NER160 (O—CH NER161 —COOCH NER162) NER163] NER164 (7a) (In formula (7a), n is an integer of 1 to 5.

*744* It was confirmed that the compound was a siloxane derivative represented by the formula:

*745* An example of the structural formula of the siloxane derivative presumed from these results is shown in the following formula (8):

[0069]

*750* As shown in.

[0070]

*754* Furthermore, from the results shown in FIG. 4, it was found that the siloxene derivative was a layered compound with an interlayer distance of 13.2 Å, and that the siloxene skeleton corresponded to the Si(111) surface of single crystal silicon.

[0071]

*760* Example 2 The siloxene derivative (160.4 mg) obtained in Example 1, anhydrous acetonitrile (5 ml), and N-(3-aminopropyl)imidazole (H<sub> 2 </sub>N-(CH<sub> 2 </sub>)<sub> 3 </sub>-[C<sub> 3 </sub>H<sub> 3 </sub>N<sub> 2 </sub>], 2 ml) were placed in a Schlenk flask and stirred while being heated at 60 ° C. for 18 hours to react the siloxene derivative with N-(3-aminopropyl)imidazole.

*765* The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm.

767 The filter cake was washed with anhydrous tetrahydrofuran (anhydrous THF) and then vacuum dried at room temperature for 1 hour to obtain a powder (190.8 mg).

[0072]

772 The infrared absorption spectrum and the X-ray diffraction pattern of the obtained powder are shown in FIG. 5 and FIG. 6, respectively.
774 In the infrared absorption spectrum shown in FIG. 5, a peak due to the Si-H bond was observed near 2100 cm<sup>－1</sup>, and a peak due to the stretching vibration mode of the C-H bond of the imidazole ring was observed near 3150 cm<sup>－1</sup>, which suggests that the methyl glycolate bonded to the siloxane skeleton was selectively amidated.
778 Therefore, the obtained powder had the following composition formula (9): Si NER173 H NER174 (O—CH NER175 —CONH—(CH NER176 —) NER177 —[C NER178 H NER179 N NER180 —]) NER181 (9) (In formula (9), 1≦a≦5.
781 ) and the following structural formula (9a): [Si<sub>6</sub>H<sub>n</sub>(O-CH<sub>2</sub>-CONH-(CH<sub>2</sub>)<sub>3</sub>-[C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>])<sub>6－n</sub>]<sub>m</sub> (9a) (In formula (9a), n is an integer of 1 to 5.
785 ) was found to be a siloxane composite material.
786 An example of the structural formula of the siloxene composite material inferred from these results is the following formula (10):

[0074]

791 As shown in.

[0075]

795 Furthermore, in the X-ray diffraction pattern shown in FIG. 6, a peak believed to correspond to the interlayer was observed, and it was found that the obtained siloxene composite material was a layered compound with an interlayer distance of 25.4 Å.
798 This interlayer distance is larger than the interlayer distance (13.2 Å) of the siloxene derivative obtained in Example 1, and it is believed that the interlayer distance is expanded by the propylimidazole group introduced before the amide bond.

[0076]

804 Example 3 The siloxene derivative (62.2 mg) obtained in Example 1, anhydrous acetonitrile (5 ml), anhydrous pyridine (1 ml), and 1-aminopyrrole (H<sub>2</sub>N-[C<sub>4</sub>H<sub>4</sub>N], 68.8 mg) were placed in a Schlenk flask and stirred while being heated at 80 ° C. for 72 hours to react the siloxene derivative with 1-aminopyrrole.

*809* The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm.

*809* The filter cake was washed with anhydrous acetonitrile and then vacuum dried at room temperature for 1 hour to obtain a powder (79.5 mg).

[0077]

*816* The infrared absorption spectrum and the X-ray diffraction pattern of the obtained powder are shown in FIG. 7 and FIG. 8, respectively.

*818* In the infrared absorption spectrum shown in FIG. 7, a peak due to the Si-H bond was observed near 2100 cm<sup>— 1 </sup>, and a peak due to the stretching vibration mode of the C-H bond of the pyrrole ring was observed near 3100 cm<sup>— 1 </sup>, which suggests that the methyl glycolate bonded to the siloxane skeleton was selectively amidated.

*822* Therefore, the obtained powder had the following composition formula (11):
Si<sub> 6 </sub>H<sub> a </sub>(O—CH<sub> 2 </sub>—CONH—[C<sub> 4 </sub>H<sub> 4 </sub>N])<sub> 6 − a </sub> (11) (In formula (11), 1≦a≦5.

*825* and the following structural formula (11a):
[Si<sub> 6 </sub>H<sub> n </sub>(O—CH<sub> 2 </sub>—CONH—[C<sub> 4 </sub>H<sub> 4 </sub>N])<sub> 6 − n </sub>]<sub>m</sub> (11a) (In formula (11a), n is an integer of 1 to 5.

*829* ) was found to be a siloxane composite material.

*830* An example of the structural formula of the siloxene composite material inferred from these results is the following formula (12):

[0079]

*835* As shown in.

[0080]

*839* Furthermore, in the X-ray diffraction pattern shown in FIG. 8, a peak believed to correspond to the interlayer was observed, and it was found that the obtained siloxene composite material was a layered compound with an interlayer distance of 15.8 Å.

*842* This interlayer distance is larger than the interlayer distance (13.2 Å) of the siloxene derivative obtained in Example 1, and it is believed that the interlayer distance is expanded by the pyrrole ring introduced before the amide bond.

*845* In addition, compared to the siloxene composite material obtained in Example 2, the length of the introduced amine compound was shorter, and therefore the interlayer distance was shorter.

[0081]

Example 4 The siloxene derivative (46.7 mg) obtained in Example 1, anhydrous acetonitrile (3 ml), and imidazole ([C<sub> 3 </sub>H<sub> 4 </sub>N<sub> 2 </sub>], 18.7 mg) were placed in a Schlenk flask and stirred while being heated at 60 ° C. for 24 hours to react the siloxene derivative with imidazole.
The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm.
The filter cake was washed with anhydrous acetone and then vacuum dried at room temperature for 1 hour to obtain a powder (62.8 mg).

## [0082]

The infrared absorption spectrum and the X-ray diffraction pattern of the obtained powder are shown in FIG. 9 and FIG. 10, respectively.
In the infrared absorption spectrum shown in FIG. 9, a peak due to the Si-H bond was observed near 2100 cm<sup>— 1 </sup>, and a peak due to the stretching vibration mode of the C-H bond of the imidazole ring was observed near 3100 cm<sup>— 1 </sup>, which suggests that the methyl glycolate bonded to the siloxane skeleton was selectively amidated.
Therefore, the obtained powder had the following composition formula (13): SiNER215HNER216(O-CHNER217-CO[CNER218HNER219NNER220])NER221 (13), where 1≦a≦5.
) and the following structural formula (13a): [Si<sub> 6 </sub>H<sub> n </sub>(O—CH<sub> 2 </sub>—CO[C<sub> 3 </sub>H<sub> 3 </sub>N<sub> 2 </sub>])<sub> 6 − n </sub>]<sub>m</sub> (13a) (In formula (13a), n is an integer of 1 to 5.
) was found to be a siloxane composite material.
An example of the structural formula of the siloxene composite material inferred from these results is the following formula (14):

## [0084]

As shown in.

## [0085]

Furthermore, in the X-ray diffraction pattern shown in FIG. 10, a peak believed to correspond to the interlayer was observed, and it was found that the obtained siloxene composite material was a layered compound with an interlayer distance of 16.5 Å.
This interlayer distance is larger than the interlayer distance (13.2 Å) of the siloxene derivative obtained in Example 1, and it is believed that the imidazole ring introduced before the amide bond spreads the space between the layers.
In addition, compared to the siloxene composite material obtained in Example 2, the length of the introduced compound was shorter, and therefore the interlayer distance was shorter.

893 Furthermore, in the X-ray diffraction pattern shown in FIG. 10, a peak corresponding to an interlayer distance of 4.94 Å was observed.

893 This is believed to be the distance at which the imidazole rings are stacked.

## [0086]

899 Example 5 The siloxene derivative (202.5 mg) obtained in Example 1, anhydrous acetonitrile (2 ml), anhydrous pyridine (2 ml), and pyrrole ([C<sub> 4 </sub>H<sub> 5 </sub>N], 3 ml) were placed in a Schlenk flask and stirred while being heated at 80 ° C. for 72 hours to react the siloxene derivative with pyrrole.

903 The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm.

905 The filter cake was washed with anhydrous acetone and then vacuum dried at room temperature for 1 hour to obtain a powder (214.8 mg).

## [0087]

910 The infrared absorption spectrum and the X-ray diffraction pattern of the obtained powder are shown in FIG. 11 and FIG. 12, respectively.

912 In the infrared absorption spectrum shown in FIG. 11, a peak due to the Si-H bond was observed near 2100 cm<sup>－ 1 </sup>, and a peak due to the stretching vibration mode of the C-H bond of the pyrrole ring was observed near 3100 cm<sup>－ 1 </sup>, which suggests that the methyl glycolate bonded to the siloxene skeleton was selectively amidated.

916 Therefore, the obtained powder had the following composition formula (15): SiNER234HNER235(O-CHNER236-CO[CNER237HNER238N])NER239(15), where 1≦a≦5.

918 ) and the following structural formula (15a): [Si<sub> 6 </sub>H<sub> n </sub>(O—CH<sub> 2 </sub>—CO[C<sub> 4 </sub>H<sub> 4 </sub>N])<sub> 6 － n </sub>]<sub>m</sub> (15a) (In formula (15a), n is an integer of 1 to 5.

921 ) was found to be a siloxane composite material.

922 An example of the structural formula of the siloxene composite material inferred from these results is the following formula (16):

## [0089]

927 As shown in.

## [0090]

931 Furthermore, in the X-ray diffraction pattern shown in FIG. 12, a peak believed to correspond to the interlayer was observed, and it was found that the obtained siloxene composite material was a layered compound with an interlayer distance of 16.1 Å.

934 This interlayer distance is larger than the interlayer distance (13.2 Å) of the siloxene

derivative obtained in Example 1, and it is believed that the interlayer distance is expanded by the pyrrole ring introduced before the amide bond. In addition, compared to the siloxene composite material obtained in Example 3, the length of the introduced compound was equivalent, and therefore the interlayer distance was also approximately the same. Furthermore, in the X-ray diffraction pattern shown in FIG. 12, a peak corresponding to an interlayer distance of 4.94 Å was observed. This is believed to be the distance at which the pyrrole rings are stacked.

[0091]

Example 6 The siloxene derivative (155.4 mg) obtained in Example 1, anhydrous acetonitrile (3 ml), anhydrous pyridine (0.5 ml), and 2-(2-aminoethyl)thiophene ($H_2N-(CH_2)_2-[C_4H_3S]$, 158.1 mg) were placed in a Schlenk flask and stirred while heating at 60 ° C. for 18 hours to react the siloxene derivative with 2-(2-aminoethyl)thiophene. The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm. The filter cake was washed with anhydrous acetone and then vacuum dried at room temperature for 1 hour to obtain a powder (192.3 mg).

[0092]

The infrared absorption spectrum and the X-ray diffraction pattern of the obtained powder are shown in FIG. 13 and FIG. 14, respectively. In the infrared absorption spectrum shown in FIG. 13, a peak due to the Si-H bond was observed near 2100 cm$^{-1}$, and a peak due to the stretching vibration mode of the C-H bond of the thiophene ring was observed near 3100 cm$^{-1}$, which suggests that the methyl glycolate bonded to the siloxene skeleton was selectively amidated. Therefore, the obtained powder had the following composition formula (17): SiNER254HNER255(O-CHNER256-CONH-(CHNER257)NER258-[CNER259HNER260S])NER261(17), where 1≦a≦5. ) and the following structural formula (17a): $[Si_6H_n(O—CH_2—CONH—(CH_2)_2—[C_4H_3S])_{6-n}]_m$ (17a) (In formula (17a), n is an integer of 1 to 5. ) was found to be a siloxane composite material. An example of the structural formula of the siloxene composite material inferred from these results is the following formula (18):

[0094]

As shown in.

[0095]

Furthermore, in the X-ray diffraction pattern shown in FIG. 14, two peaks considered to correspond to the interlayer space were observed, and it was found that the obtained siloxene composite material was a layered compound with interlayer distances of 18.0 Å and 17.1 Å. These interlayer distances are larger than the interlayer distance (13.2 Å) of the siloxene derivative obtained in Example 1, and it is believed that the interlayer distance is expanded by the ethylthiophene group introduced before the amide bond.

[0096]

Example 7 The siloxene derivative (25.5 mg) obtained in Example 1, anhydrous acetonitrile (3 ml), and 1,2-diaminododecane (H<sub> 2 </sub>N-(CH<sub> 2 </sub>)<sub> 1 2 </sub>-NH<sub> 2 </sub>, 168.5 mg) were placed in a Schlenk flask and stirred while being heated at 60 ° C. for 18 hours to react the siloxene derivative with 1,2-diaminododecane. The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm. The filter cake was washed with anhydrous acetone and then vacuum dried at room temperature for 1 hour to obtain a compound having the following composition formula (19): SiNER275HNER276(O-CHNER277-CONH-(CHNER278)NER279)NER280(19), where $1 \leqq a \leqq 5$. ) and the following structural formula (19a): [Si<sub> 6 </sub>H<sub> n </sub>(O—CH<sub> 2 </sub>—CONH—(CH<sub> 2 </sub>)<sub> 1 2 </sub>)<sub> 6 − n </sub>]<sub>m</sub> (19a) (In formula (19a), n is an integer of 1 to 5. As a result, 32.9 mg of a siloxane composite material represented by the formula: An example of the presumed structural formula of the siloxene composite material is shown below in formula (20):

[0098]

In formula (20), * represents a bonding site with an adjacent siloxene skeleton. ) as shown.

[0099]

The X-ray diffraction pattern of the resulting siloxene composite material is shown in FIG. In the X-ray diffraction pattern shown in FIG. 15, a peak believed to correspond to the interlayer was observed, and it was found that the obtained siloxene composite material was a layered compound with an interlayer distance of 19.7 Å.

1022 This interlayer distance was approximately equal to the interlayer distance when the siloxene derivative obtained in Example 1 was crosslinked with 1,2-diaminododecane.

1025 Furthermore, in the region of 2θ=18 to 27 ° in the X-ray diffraction pattern shown in FIG. 15, a peak thought to be due to the crystalline orientation of dodecyl groups within the layers was observed.

## [0100]

1031 Example 8 The siloxene derivative (85.4 mg) obtained in Example 1, anhydrous acetonitrile (3 ml), anhydrous pyridine (1 ml), and n-decylamine (CH-NER-(CH-NER)-NER-NH-NER, 354.8 mg) were placed in a Schlenk flask and stirred while being heated at 80 ° C. for 13 hours to react the siloxene derivative with n-decylamine.

1035 The resulting suspension was filtered in a glove box using a Teflon (registered trademark) filter with a pore size of 1 μm.

1037 The filter cake was washed with anhydrous acetone and then vacuum dried at room temperature for 1 hour to obtain a compound having the following composition formula (21): SiNER292HNER293(O-CHNER294-CONH-CNER295HNER296)NER297(21), where 1≦a≦5.

1041 ) and the following structural formula (21a): [Si NER298 H NER299 (O—CH NER300 —CONH—C NER301 H NER302) NER303] NER304 (21a) (In formula (21a), n is an integer of 1 to 5.

1044 As a result, 108.4 mg of a siloxane composite material represented by the formula:

1045 An example of the presumed structural formula of the siloxene composite material is shown below in formula (22):

## [0102]

1050 As shown in.

## [0103]

1054 The X-ray diffraction pattern, the fluorescence spectrum (excitation wavelength: 275 nm) and the excitation spectrum (fluorescence wavelength: 420 nm) of the obtained siloxene composite material are shown in Figures 16 to 18, respectively.

1057 In the X-ray diffraction pattern shown in FIG. 16, a peak believed to correspond to the interlayer was observed, and it was found that the obtained siloxene composite material was a layered compound with an interlayer distance of 28.6 Å.

1060 This interlayer distance is larger than the interlayer distance (13.2 Å) of the siloxene derivative obtained in Example 1, and it is believed that the interlayer distance is expanded by the dodecyl group introduced before the amide bond.

[0104]

Comparative Example 1 According to the method described in A. Weiss et al. (Z. Naturforsch. 1979, vol. 34b, pp. 25-30), a siloxane composite having an interlayer distance substantially equal to the interlayer distance (28.6 Å) of the siloxane composite material obtained in Example 8 was prepared, the following composition formula (23): Si<sub>６</sub>H<sub>ａ</sub>(O-C<sub>１２</sub>H<sub>２１</sub>)<sub>６－ａ</sub> (23) (wherein 1≦a≦5).

) and the following structural formula (23a): [Si<sub>６</sub>H<sub>ｎ</sub>(O-C<sub>１２</sub>H<sub>２１</sub>)<sub>６－ｎ</sub>]<sub>ｍ</sub> (23a) (In formula (23a), n is an integer of 1 to 5.

A siloxene derivative represented by the formula:

[0105]

That is, calcium disilicide (142.8 mg) and n-dodecanol (5.0 g) were mixed under a nitrogen atmosphere, and a dioxane solution of hydrogen chloride (4 mol/L, 25 ml) was added thereto, and calcium disilicide and n-dodecanol were reacted at room temperature for 24 hours.

The resulting suspension was filtered, and the filter cake was washed with anhydrous acetone and dried in vacuum at 25 ° C. for 1 hour to obtain a pale yellow powder (209.8 mg).

[0106]

The fluorescence spectrum (excitation wavelength: 275 nm) and the excitation spectrum (fluorescence wavelength: 420 nm) of the resulting pale yellow powder (the siloxene derivative) are shown in Figures 17 and 18, respectively.

An example of the presumed structural formula of the siloxane derivative is shown below in formula (24):

[0108]

As shown in.

[0109]

As is clear from the results shown in FIG. 17, the siloxene composite material obtained in Example 8 and the siloxene derivative obtained in Comparative Example 1 exhibited almost the same fluorescence spectrum.

On the other hand, as is clear from the results shown in FIG. 18, the siloxene composite material obtained in Example 8 had higher absorbance in the short wavelength region (ultraviolet region, particularly wavelengths of 270 nm and 300 nm) than the siloxene derivative obtained in Comparative Example 1.

1109 This is believed to be because the ultraviolet absorption band due to the amide group in the siloxane composite material is involved in the fluorescence excitation of silicon (maximum fluorescence wavelength: 420 nm).

## [0110]

1117 As described above, according to the present invention, it is possible to obtain a siloxene composite material in which an organic group having an amide group is bonded to a siloxene skeleton.

1120 This siloxene composite material has an absorption band in the ultraviolet region derived from the amide group, has a wide excitation wavelength absorption band, and exhibits fluorescent properties similar to those of silicon.

1123 Therefore, the siloxene composite material of the present invention is expected to be used as an optical device material that can effectively utilize sunlight.

## [0111]

1128 Furthermore, according to the present invention, it becomes possible to easily allow guest molecules and guest ions to enter and exit between the layers of the siloxene composite material without causing any drastic change in the shape of the siloxene composite material.

1132 Therefore, while a problem with conventional electrode materials for electric double layer capacitors is the change in volume caused by the insertion and desorption of ions between the layers during charging and discharging, it is expected that this problem will be solved by using the siloxene composite material of the present invention.

## [0112]

1139 Furthermore, according to the present invention it is possible to prepare a siloxene composite material having a framework corresponding to the Si(111) surface of single crystal silicon.

1142 Siloxene composite materials having such a skeleton can be used as semiconductor thin films by forming them into thin films.

## [0113]

1147 As described above, the siloxene composite material of the present invention is expected to be applicable to a variety of fields, such as semiconductor materials, electric and electronic materials, optical integration materials, electrode materials for solar cells and secondary batteries, and light-emitting device materials.