

STABILIZER FOR SUPPRESSING GENERATION OF SILANE FROM A POLYSILANE COMPOSITION AND METHOD FOR SUPPRESSING GENERATION OF SILANE

5 BACKGROUND OF THE INVENTION

TECHNICAL FIELD

[0001] The present invention relates to a stabilizer for suppressing generation of silane from a polysilane composition and a method for suppressing generation of silane. Further, the present invention relates to a method for inactivating a polysilane, and a polysilane inactivated treatment composition.

15 BACKGROUND ART

[0002] Silicon films have relatively high hardness and sealability, and are used for various applications in semiconductor manufacturing field. In specific, silicon films are used for applications such as hard coating films of substrates, circuits and the like, gas barrier films, and substrate strength enhancement films.

High molecular weight polysilane can form a thin film in a simple process comprising applying a coating solution and heating, without a vacuum state, due to their solubility in solvents. Polysilane can be used for filling fine grooves of interlayer insulation films of semiconductor devices by liquid capillary action.

[0003] It is known that polysilane can be decomposed to generate silane gas (SiH_4 gas) after a long storage.

30 SiH_4 gas has very highly volatility and can ignite spontaneously in air. From the viewpoint of safety, such silane gas has been treated by a method such as hydrolysis by an alkali solution, adsorption removal using metal oxide, or combustion, for a long time.

35 However, all these treating methods need to use equipment. Further, these methods are to treat

35 However, all these treating methods need to use
equipment. Further, these methods are to treat

generated silane and not to suppress silane generation.
Thus, there is a danger until the treatment is completed.

[0004] When a coating solution comprising polysilane is applied to form a thin film, for example, spin coating method can be employed. When the solution is coated on a substrate by spin coating method, edge beads are formed on the periphery of the substrate and, in addition, the solution sneaks to the backside of the substrate. In order to prevent the coating film from becoming nonuniform in thickness at the peripheral part of the substrate due to the presence of the edge beads, in general, edge bead removal treatment (hereinafter referred to as "EBR treatment") is carried out. After coating of the coating solution, a treating solvent is coated or sprayed on the surface side of the substrate to remove (edge cut) the coating film at its peripheral part. In addition, back rinsing is also carried out for removing the polysilane which sneaked and was deposited on the backside of the substrate to clean the backside. This rinse solution after back rinsing comprises polysilane.

Further, the coating film is required to be removed from the substrate depending on the necessity of conducting subsequent treatment, and the polysilane deposited on the coating device such as a spin coater is required to be washed or removed. The remover and the like after such treatment comprises polysilane.

Such a rinse solution and remover comprising polysilane can be temporarily retained in a waste liquid tank. In the waste liquid tank, silane gas is generated, and therefore the silane gas is required to be treated as described above.

[0005] From the viewpoint of meeting demands for higher-accuracy quality control, reliable safety and the like in recent years, there is a need for a method that can use polysilane in a safer and simpler manner.

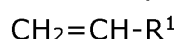
SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

5 [0006] It is an object of the present invention to provide a stabilizer for suppressing generation of silane from a polysilane composition and a method for suppressing generation of silane. Further, it is an object of the present invention to provide a method for inactivating a
10 polysilane, and a polysilane inactivated treatment composition.

MEANS FOR SOLVING THE PROBLEMS

[0007] The stabilizer for suppressing generation of silane
15 from a polysilane composition according to the present invention is represented by the following formula:



wherein R^1 is

C_{3-20} linear, branched or cyclic alkyl group,
20 C_{2-15} linear or branched alkenyl group or
 C_{7-20} aryl group substituted with alkenyl group.

[0008] The use of the stabilizer according to the present invention, wherein generation of silane from a polysilane composition is suppressed by adding above mentioned
25 stabilizer.

[0009] The method for suppressing generation of silane according to the present invention, comprising making above mentioned stabilizer coexist with a polysilane.

[0010] The method for inactivating a polysilane containing
30 waste liquid according to the present invention comprising mixing the polysilane containing waste liquid with above mentioned stabilizer.

[0011] A polysilane inactivated treatment composition according to the present invention comprising above
35 mentioned stabilizer and a solvent.

EFFECTS OF THE INVENTION

[0012] According to the present invention, generation of silane from a polysilane composition is suppressed and silane concentration can be kept low in a simple manner.

5

DETAILED DESCRIPTION OF THE INVENTION

MODE FOR CARRYING OUT THE INVENTION

[0013] Embodiments of the present invention are described below in detail. Hereinafter, symbols, units, abbreviations, and terms have the following meanings in the present specification unless otherwise specified.

10

15

20

In the present specification, unless otherwise specifically mentioned, the singular includes the plural and "one" or "that" means "at least one". In the present specification, unless otherwise specifically mentioned, an element of a concept can be expressed by a plurality of species, and when the amount (for example, mass % or mol%) is described, it means sum of the plurality of species. "And/or" includes a combination of all elements and also includes single use of the element.

25

[0014] In the present specification, when numerical ranges are indicated using "to" or "-", they include both end points, and the units thereof are common. For example, 5 to 25 mol % means 5 mol % or more and 25 mol % or less.

30

[0015] In the present specification, the hydrocarbon means one including carbon and hydrogen, and optionally including oxygen or nitrogen. The hydrocarbyl group means a monovalent or divalent or higher valent hydrocarbon.

35

In the present specification, the aliphatic hydrocarbon means a linear, branched or cyclic aliphatic hydrocarbon, and the aliphatic hydrocarbon group means a monovalent or divalent or higher valent

aliphatic hydrocarbon. The aromatic hydrocarbon means a hydrocarbon comprising an aromatic ring which may optionally not only comprise an aliphatic hydrocarbon group as a substituent but also be condensed with an alicycle. The aromatic hydrocarbon group means a monovalent or divalent or higher valent aromatic hydrocarbon. Further, the aromatic ring means a hydrocarbon comprising a conjugated unsaturated ring structure, and the alicycle means a hydrocarbon comprising a ring structure but no conjugated unsaturated ring structure.

[0016] In the present specification, the alkyl means a group obtained by removing any one hydrogen from a linear or branched, saturated hydrocarbon and includes a linear alkyl and branched alkyl, and the cycloalkyl means a group obtained by removing one hydrogen from a saturated hydrocarbon comprising a cyclic structure and includes a linear or branched alkyl in the cyclic structure as a side chain, if necessary.

[0017] In the present specification, the alkenyl means a group obtained by removing any one hydrogen from carbon of linear or branched hydrocarbon having one carbon-carbon double bond.

[0018] In the present specification, the aryl means a group obtained by removing any one hydrogen from an aromatic hydrocarbon. The alkylene means a group obtained by removing any two hydrogen from a linear or branched, saturated hydrocarbon. The arylene means a hydrocarbon group obtained by removing any two hydrogen from an aromatic hydrocarbon.

[0019] In the present specification, the description such as "C_{x-y}", "C_x-C_y" and "C_x" means the number of carbons in the molecule or substituent group. For example, C₁₋₆ alkyl means alkyl having 1 to 6 carbons (such as methyl, ethyl, propyl, butyl, pentyl and hexyl). Further, the fluoroalkyl as used in the present specification refers to

one in which one or more hydrogen in alkyl is replaced with fluorine, and the fluoroaryl is one in which one or more hydrogen in aryl are replaced with fluorine.

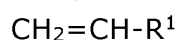
[0020] In the present specification, when a polymer comprises plural types of repeating units, these repeating units copolymerize. These copolymerizations can be any of alternating copolymerization, random copolymerization, block copolymerization, graft copolymerization, or any mixture thereof.

10 In the present specification, "%" represents weight % and "ratio" represents ratio by weight.

[0021] In the present specification, Celsius is used as the temperature unit. For example, 20 degrees means 20 degrees Celsius.

15 [0022] <Stabilizer>

The stabilizer according to the present invention is used for suppressing generation of silane for a polysilane composition, and represented by the following formula:



20 wherein R^1 is

C_{3-20} linear, branched or cyclic alkyl group,
 C_{2-15} linear or branched alkenyl group or
 C_{7-20} aryl group substituted with alkenyl group.

[0023] Preferably, R^1 is

25 (i) C_{3-20} linear or branched alkyl group,
(ii) C_{5-8} cyclic alkyl group,
(iii) C_{3-15} linear alkenyl group having an unsaturated bond at a terminal, or
(iv) C_{7-10} phenyl group substituted with alkenyl group
30 having an unsaturated bond at a terminal.

[0024] When R^1 is (i), examples of the stabilizer include 1-pentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3,3-dimethyl-1-butene, 1-heptene, 5-methyl-1-hexene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

35

[0025] When R^1 is (ii), the stabilizer is preferably 5

membered ring or 6 membered ring, and examples of the stabilizer include vinylcyclopentane, vinylcyclohexane, and allylcyclohexane.

5 [0026] When R^1 is (iii), examples of the stabilizer include 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, and 1,11-dodecadiene.

10 [0027] When R^1 is (iv), examples of the stabilizer include 1,2-divinylbenzene, 1,3-divinylbenzene, and 1,4-divinylbenzene.

[0028] The stabilizer according to the present invention can be a mixture containing 2 or more kinds of the above described compounds.

15 [0029] The stabilizer according to the present invention can generally be applied to any polysilane composition. Polysilane composition can consist only of polysilane, and can comprise components other than polysilane, for example a solvent.

20 [0030] The polysilane that can be stabilized by the stabilizer according to the present invention is not particularly limited as long as it is a linear, branched or cyclic compound having a main chain consisting of only Si-Si bonds. The polysilane having branched structures is preferred because it is more likely to exert the effect of suppressing generation of silane due to its more
25 terminal groups.

The polysilane is preferably polyperhydrosilane because the effect of the stabilizer according to the present invention becomes higher.

30 The mass molecular weight of polysilane is not particularly limited. When the mass molecular weight of polysilane is 300 to 10,000, more preferably 500 to 5,000, it is preferred because the effect of the stabilizer according to the present invention is higher. The mass
35 average molecular weight is a mass average molecular weight in terms of polystyrene, and it can be measured

by gel permeation chromatography based on polystyrene.

[0031] Generation of silane from a polysilane composition can be suppressed by adding the stabilizer according to the present invention to the polysilane composition to make the stabilizer coexist with the polysilane. Without wishing to be bound by theory, it is believed that this is due to the following reason.

5 The stabilizer according to the present invention has a C-C double bond at a terminal. Polysilane decomposes to form a silylene radical, and the silylene radical react with the other polysilane to increase the molecular weight of the polysilane. Silylene radical is likely to bond with a compound having a double bond to form a stable compound. Thus, making the stabilizer according to the present invention coexist with polysilane can prevent further polymerization of polysilane due to the reaction of formed silylene radical with the stabilizer. The higher the molecular weight of polysilane is, the more silane gas is generated in a short period time. Therefore, silane gas generation amount can be reduced by suppressing the further polymerization reaction using the stabilizer according to the present invention.

15 [0032] The number of moles of the stabilizer according to the present invention is preferably 10 to 1,000 mol %, and more preferably 50 to 300 mol %, based on the number of moles of Si contained in polysilane.

[0033] <Polysilane inactivated treatment composition>

30 The polysilane inactivated treatment composition according to the present invention (hereinafter sometimes referred to as "treatment composition") comprises above described stabilizer and a solvent. The polysilane inactivated treatment composition according to the present invention can be suitably used as an edge bead removal treatment composition or a waste liquid

35

treatment composition.

[0034] The solvent is selected from those which uniformly dissolve the stabilizer. In particular, examples of the solvent include ethylene glycol monoalkyl ethers, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether and ethylene glycol monobutyl ether; diethylene glycol dialkyl ethers, such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dipropyl ether and diethylene glycol dibutyl ether; ethylene glycol alkyl ether acetates, such as methyl cellosolve acetate and ethyl cellosolve acetate; propylene glycol monoalkyl ethers, such as propylene glycol monomethyl ether (PGME) and propylene glycol monoethyl ether; propylene glycol alkyl ether acetates such as propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether acetate and propylene glycol monopropyl ether acetate; aromatic hydrocarbons, such as benzene, toluene, xylene and mesitylene; ketones, such as methyl ethyl ketone, acetone, methyl amyl ketone, methyl isobutyl ketone and cyclohexanone; alcohols, such as isopropanol and propanediol; and alicyclic hydrocarbons, such as cyclooctane and decalin. Preferred are cyclooctane, toluene, decalin and mesitylene.

These solvents can be used alone or in combination of two or more of any of these.

[0035] The mixing ratio of the solvent depends on its applications. The ratio of the other components other than the solvent is preferably 1 to 96 mass %, and more preferably 2 to 60 mass %.

[0036] In the treatment composition according to the present invention, if necessary, further compounds can be comprised to the extent that the effects of the present invention are not impaired. The ratio of components other than the stabilizer and solvent is

preferably 10 mass % or less, and more preferably 5 mass % or less.

[0037] Hereinafter, the present invention is explained with reference to Examples. These Examples are for
5 explanation and are not intended to limit the scope of the present invention.

In the following description, "part" is on a mass basis unless otherwise specified.

[0038] The steps in which polysilane is treated in the
10 following synthesis examples and Examples are all carried out in a glove box controlled to have an oxygen concentration of 1.0 ppm or less and a dew point temperature of -76.0°C or less under a nitrogen atmosphere.

15 [0039] Synthesis of polysilane

A stirrer tip is placed in a 50 mL screw tube, and 30 g (0.166 mol) of cyclohexasilane is added thereto and stirred using a stirrer. Here, 8.5 J /cm² of ultraviolet ray having a wavelength of 365 nm using a mercury
20 xenon lamp as a light source is irradiated. After the ultraviolet irradiation, it is dissolved in cyclooctane, and cyclooctane is added so that the solid concentration is 19 mass %. The mass average molecular weight of the obtained polysilane is 800.

25 [0040] Examples 1 to 4 and Comparative examples 1 and 2

To a 20mL glass syringe vial (ASLAB2017-V, SCW223: AS ONE Corporation), 0.2 g of the cyclooctane solution obtained from the synthesis example and the stabilizer described in Table 1 are added. Then,
30 cyclooctane is added so that the concentration of the polysilane is 10 mass % based on the total mass of the solution. Noted that comparative example 1 contains no stabilizer.

The gas phase of the syringe vial is air and sealed.
35 Three syringe vials which are same conditions are prepared, and they are stored at 23±1°C for 72 hours.

After 72 hours, the silane concentration in the gas-phase is measured by gas chromatography. An average value of the 3 measured values is used as a measured value.

Table 1

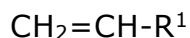
	Stabilizer	Content of the stabilizer based on the number of moles of Si in polysilane (mol%)	Silane concentration after 72 hours (ppm)
Example 1	1-octene	200	8
Example 2	1-octene	100	9
Example 3	divinylbenzene	200	6
Example 4	1,5-hexadiene	200	9
Comparative example 1	-	-	2,000
Comparative example 2	styrene	200	4,900

5 [0041] Measurement of silane concentrations

The silane concentration in the gas-phase is measured by GC-8A Gas Chromatograph (Shimadzu Corporation), Carrier gas: N₂, Column: PoraPak Q80/100, Detector: TCD. Calibration is carried out with 1000 ppm silane standard gas.

Patent Claims

1. Use of a stabilizer represented by the following formula in suppressing generation of silane from a polysilane composition:



wherein R^1 is

C_{3-20} linear, branched or cyclic alkyl group,

C_{2-15} linear or branched alkenyl group or

C_{7-20} aryl group substituted with alkenyl group, and

wherein generation of silane from the polysilane composition is suppressed by adding the stabilizer.

2. The use according to claim 1, wherein R^1 is

C_{3-20} linear or branched alkyl group,

C_{5-8} cyclic alkyl group,

C_{3-15} linear alkenyl group having an unsaturated bond at a terminal, or

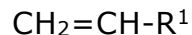
C_{7-10} phenyl group substituted with alkenyl group having an unsaturated bond at a terminal.

3. The use according to claim 1 or 2, wherein the stabilizer is selected from the group consisting of 1-pentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3,3-dimethyl-1-butene, 1-heptene, 5-methyl-1-hexene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, vinylcyclopentane, vinylcyclohexane, allylcyclohexane, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,2-divinylbenzene, 1,3-divinylbenzene, and 1,4-divinylbenzene.

4. The use according to one or more of claims 1 to 3, wherein the polysilane is polyperhydrosilane.

5. A method of suppressing generation of silane, comprising making a stabilizer represented by the following formula coexist

with a polysilane,



wherein R^1 is

C_{3-20} linear, branched or cyclic alkyl group,

C_{2-15} linear or branched alkenyl group or

C_{7-20} aryl group substituted with alkenyl group.

6. The method according to claim 5, wherein R^1 is

C_{3-20} linear or branched alkyl group,

C_{5-8} cyclic alkyl group,

C_{3-15} linear alkenyl group having an unsaturated bond at a terminal, or

C_{7-10} phenyl group substituted with alkenyl group having an unsaturated bond at a terminal.

7. The method according to claim 5 or 6,

wherein the stabilizer is selected from the group consisting of 1-pentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3,3-dimethyl-1-butene, 1-heptene, 5-methyl-1-hexene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, vinylcyclopentane, vinylcyclohexane, allylcyclohexane, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,2-divinylbenzene, 1,3-divinylbenzene, and 1,4-divinylbenzene.

8. The method according to one or more of claims 5 to 7,

wherein the polysilane is polyperhydrosilane.