

POLYSILOXANE COMPOSITION

BACKGROUND OF THE INVENTION

5 TECHNICAL FIELD

[0001] The present invention relates to a polysiloxane composition. Further, the present invention relates to a method for manufacturing a film using the same, a film using the same, and a method for manufacturing an electronic device comprising the film.

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BACKGROUND ART

[0002] Polysiloxane is known to have resistance to elevated temperature. When a cured film is formed from a composition containing a polysiloxane, the coating film is heated at an elevated temperature to rapidly proceed with a condensation reaction of silanol groups in the polysiloxane and a reaction of a polymer having an unsaturated bond to cure the film. If unreacted reactive groups remain, they may react with the chemicals to be used in the device manufacturing process. Due to the influence on other materials in the substrate and from the device conditions, the development of a composition containing polysiloxane capable of being cured at a lower temperature has been desired.

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[0003] For the purpose of curing an epoxy resin at a low temperature, the combination of an epoxy resin, an anionic polymerizable curing agent and an ionic liquid has been proposed (for example, Patent Document 1), and in a comparative example where no anionic polymerizable curing agent is contained, any curing is not caused.

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35 PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004] [Patent document 1] JP 2019-14781 A

SUMMARY OF THE INVENTION

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PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] The present invention has been made in view of the above circumstances, and provides a polysiloxane composition capable of being cured at a low temperature and having good storage stability. Further, its object is to provide, using the same, methods for manufacturing cured film and an electronic device.

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MEANS FOR SOLVING THE PROBLEMS

15 [0006] The polysiloxane composition according to the present invention comprises:

- (I) a polysiloxane,
- (II) an ionic liquid,
- (III) an acid, and
- 20 (IV) a solvent.

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[0007] Further, the method for manufacturing a cured film according to the present invention comprises applying the above-mentioned composition above a substrate to form a coating film, and heating the coating film.

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[0008] Further, the method for manufacturing an electronic device according to the present invention comprises the above-mentioned method for manufacturing a cured film.

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EFFECTS OF THE INVENTION

[0009] The polysiloxane composition according to the present invention can be cured at a lower temperature than the temperature range adopted for a general thermally curable composition. The polysiloxane composition according to the present invention is good in storage stability. And the obtained cured film has a

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small amount of film loss and is also good in film thickness uniformity. Additionally, it has good filling properties even when applied on a substrate having a high aspect ratio. Since the obtained cured film has good planarization and electrical insulation characteristics, it can be suitably used for an interlayer insulating film of semiconductor devices, a passivation film, a substrate planarization film, an anti-reflective film, an optical filter, a high-intensity light emitting diode, a touch panel, a solar cell and an optical device such as an optical waveguide device.

DETAILED DESCRIPTION OF THE INVENTION

15 MODE FOR CARRYING OUT THE INVENTION

[0010] [Definition]

Unless otherwise specified in the present specification, the definitions and examples described in this paragraph are followed.

20 The singular form includes the plural form and "one" or "that" means "at least one". 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.

25 "And/or" includes a combination of all elements and also includes single use of the element.

When a numerical range is indicated using "to" or "-", it includes both endpoints and units thereof are common. For example, 5 to 25 mol % means 5 mol % or more and 25 mol % or less.

30 The descriptions such as "C_{x-y}", "C_x-C_y" and "C_x" mean the number of carbons in a molecule or substituent. For example, C₁₋₆ alkyl means an alkyl chain having 1 or more and 6 or less carbons (methyl, ethyl, propyl, butyl, pentyl, hexyl etc.).

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When a polymer has a plural types of repeating

units, these repeating units copolymerize. These copolymerization may be any of alternating copolymerization, random copolymerization, block copolymerization, graft copolymerization, or a mixture thereof. When a polymer or resin is represented by a structural formula, n, m or the like that is attached next to parentheses indicate the number of repetitions.

Celsius is used as the temperature unit. For example, 20 degrees means 20 degrees Celsius.

The additive refers to a compound itself having a function thereof (for example, in the case of a base generator, a compound itself that generates a base). An embodiment in which the compound is dissolved or dispersed in a solvent and added to a composition is also possible. As one embodiment of the present invention, it is preferable that such a solvent is contained in the composition according to the present invention as the solvent (IV) or another component.

[0011] Hereinafter, embodiments of the present invention are described in detail.

[0012] Polysiloxane composition

The polysiloxane composition according to the present invention (hereinafter sometimes simply referred to as the composition) comprises (I) a polysiloxane, (II) an ionic liquid, (III) an acid, and (IV) a solvent. Hereinafter, each component contained in the composition according to the present invention is described in detail.

[0013] (I) Polysiloxane

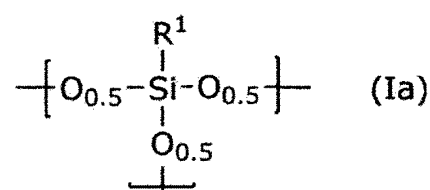
The structure of the polysiloxane used in the present invention is not particularly limited, and any polysiloxane can be selected depending on the purpose. Depending on the number of oxygen atoms bonded to a silicon atom, the skeleton structure of a polysiloxane can be classified into a silicone skeleton (the number of oxygen atoms bonded to a silicon atom is 2), a

silsesquioxane skeleton (the number of oxygen atoms bonded to a silicon atom is 3) and a silica skeleton (the number of oxygen atoms bonded to a silicon atom is 4). In the present invention, any of these may be used.

5 The polysiloxane molecule may contain a plurality of combinations of any of these skeletal structures.

[0014] Preferably, the polysiloxane used in the present invention comprises a repeating unit represented by the following formula (Ia) and a repeating unit represented by the following formula (Ib).

10 [0015] The formula (Ia) is as follows:



wherein

15 R^1 is hydrogen, a mono- to trivalent, linear, branched or cyclic, saturated or unsaturated, C_{1-30} aliphatic hydrocarbon group, or a mono- to trivalent, C_{6-30} aromatic hydrocarbon group, preferably hydrogen, linear, branched or cyclic, C_{1-6} alkyl, or C_{6-10} aryl, more preferably hydrogen, methyl, ethyl or phenyl, further preferably methyl.

20 The aliphatic hydrocarbon group and the aromatic hydrocarbon group are each unsubstituted or substituted with fluorine, hydroxy or C_{1-8} alkoxy.

25 In the aliphatic hydrocarbon group and the aromatic hydrocarbon group, methylene is not replaced, or one or more methylene are replaced with oxy, imide or carbonyl, provided that R^1 is neither hydroxy nor alkoxy.

30 When R^1 is divalent or trivalent, R^1 connects each Si contained in a plurality of repeating units.

[0016] In the formula (Ia), when R^1 is a monovalent

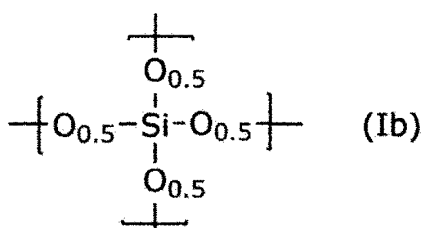
group, examples of R^1 include, in addition to hydrogen, (i) alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl and decyl, (ii) aryl such as phenyl, tolyl and benzyl, (iii) fluoroalkyl such as trifluoromethyl, 2,2,2-trifluoroethyl and 3,3,3-trifluoropropyl, (iv) fluoroaryl, (v) cycloalkyl such as cyclohexyl, (vi) nitrogen-containing groups having an amino or imide structure such as isocyanates and aminos, and (vii) oxygen-containing groups having an epoxy structure such as glycidyl, or an acryloyl or methacryloyl structure. Preferred are methyl, ethyl, propyl, butyl, pentyl, hexyl, phenyl, tolyl, glycidyl and isocyanate. As the fluoroalkyl, perfluoroalkyl, particularly trifluoromethyl and pentafluoroethyl are preferable. It is preferable that R^1 is methyl because the raw material is easily available, the film hardness after curing is high, and the film has high chemical resistance. Further, it is also preferable that R^1 is phenyl because the solubility of polysiloxane in the solvent is increased and the cured film becomes less likely to crack.

[0017] Further, when R^1 is a divalent or trivalent group, R^1 is preferably (i) a group obtained by removing two or three hydrogen from alkane such as methane, ethane, propane, butane, pentane, hexane, heptane, octane and decane, (ii) a group obtained by removing two or three hydrogen from cycloalkane such as cycloheptane, cyclohexane and cyclooctane, (iii) a group obtained by removing two or three hydrogen from an aromatic compound composed only of a hydrocarbon such as benzene and naphthalene, (iv) a group obtained by removing two or three hydrogen from a nitrogen- and/or oxygen-containing cyclic aliphatic hydrocarbon compound containing an amino group, an imino group and/or a carbonyl group, such as piperidine, pyrrolidine and isocyanurate. It is more preferably (iv), in order to improve pattern sagging and increase adhesion to the

substrate.

[0018] The number of the repeating units represented by the formula (Ia) is preferably 1% or more, more preferably 20% or more, based on the total number of the repeating units contained in the polysiloxane molecule. Since the high compounding ratio of the repeating unit represented by the formula (Ia) causes deterioration of the electrical characteristics of the cured film, decrease of the adhesion of the cured film to the contact film and decrease of the hardness of the cured film, scratches of the film surface may likely occur. Therefore, the number of the repeating units represented by the formula (Ia) is preferably 95% or less, more preferably 90% or less, based on the total number of the repeating units of the polysiloxane.

[0019] The formula (Ib) is as follows:



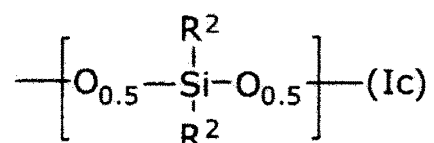
The number of the repeating units represented by the formula (Ib) is preferably 8% or more, more preferably 10 to 99%, further preferably 10 to 80%, based on the total number of the repeating units contained in the polysiloxane molecule. Since the high compounding ratio of the repeating unit represented by the formula (Ib) causes decrease of the compatibility with solvents or additives and increase of the film stress, cracks may likely. And the low compounding ratio thereof causes decrease of hardness of the cured film.

[0020] The polysiloxane used in the present invention may comprise a repeating unit other than the above, but the number thereof is preferably 20% or less, more

preferably 10% or less, based on the total number of the repeating units contained in the polysiloxane molecule.

It is also a preferred embodiment of the present invention that it contains no repeating unit other than the above.

[0021] The polysiloxane used in the present invention can further comprise a repeating unit represented by the following formula (Ic):



wherein

R² is each independently hydrogen, a mono- to trivalent, linear, branched or cyclic, saturated or unsaturated, C₁₋₃₀ aliphatic hydrocarbon group, or a mono- to trivalent, C₆₋₃₀ aromatic hydrocarbon group, preferably hydrogen, linear, branched or cyclic, C₁₋₆ alkyl, or C₆₋₁₀ aryl, more preferably hydrogen, methyl, ethyl or phenyl, further preferably methyl.

The aliphatic hydrocarbon group and the aromatic hydrocarbon group are each unsubstituted or substituted with fluorine, hydroxy or C₁₋₈ alkoxy.

In the aliphatic hydrocarbon group and the aromatic hydrocarbon group, methylene is not replaced, or one or more methylene are replaced with oxy, imide or carbonyl, provided that R² is neither hydroxy nor alkoxy.

When R² is divalent or trivalent, R² connects each Si contained in a plurality of repeating units.

By having the repeating unit of the formula (Ic), the polysiloxane can be partially formed into a straight-chain structure. However, it is preferable that the straight-chain structural portions are less because the heat resistance is lowered. In particular, the number of

the repeating unit of the formula (Ic) is 20% or less, more preferably 10% or less, based on the total number of the repeating units of polysiloxane.

[0022] The polysiloxane used in the present invention preferably has silanol at the end. Here, silanol means one in which an OH group is directly bonded to a Si skeleton, and it is one in which hydroxy is directly bonded to a silicon atom in a polysiloxane containing the above-mentioned repeating unit or the like. That is, silanol is formed by binding $-O_{0.5}H$ with $-O_{0.5}-$ of the above formula. The content of silanol in the polysiloxane varies depending on the synthesis conditions of the polysiloxane, for example, the compounding ratio of the monomers and the type of the reaction catalyst. The content of this silanol can be evaluated by quantitative infrared absorption spectrum measurement. The absorption band assigned to silanol (SiOH) appears as an absorption band having a peak in the range of $900 \pm 100 \text{ cm}^{-1}$ of the infrared absorption spectrum. The higher the content of silanol, the higher the strength of this absorption band.

[0023] When the polysiloxane is measured and analyzed by the FT-IR method, $S2/S1$ that is a ratio of the integrated intensity $S1$ of an absorption band assigned to Si-O in the range of $1100 \pm 100 \text{ cm}^{-1}$ to the integrated intensity $S2$ of an absorption band assigned to SiOH in the range of $900 \pm 100 \text{ cm}^{-1}$ is preferably 0.020 to 0.20, more preferably 0.020 to 0.15.

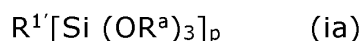
In addition, the integrated intensity of the absorption band is determined in consideration of noise in the infrared absorption spectrum. In a typical infrared absorption spectrum of polysiloxane, an absorption band assigned to Si-OH having a peak in the range of $900 \pm 100 \text{ cm}^{-1}$ and an absorption band assigned to a Si-O having a peak in the range of $1100 \pm 100 \text{ cm}^{-1}$ are confirmed. The integrated intensity of

these absorption bands can be measured as an area taking account of a baseline for which noise and the like are considered. Incidentally, there is a possibility that the foot of the absorption band assigned to Si-OH and the foot of the absorption band assigned to Si-O are overlapped; however, in such a case, the wavenumber corresponding to the minimal point between the two absorption bands in the spectrum is set as their boundary. The same applies to the case where the foot of the other absorption band overlaps with the foot of the absorption band assigned to Si-OH or Si-O.

[0024] The mass average molecular weight of the polysiloxane used in the present invention is preferably 500 to 10,000, more preferably 500 to 4,000 in terms of solubility in an organic solvent, coatability above a substrate, and solubility in an alkaline developer, and further preferably 1,000 to 3,000. Here, the mass average molecular weight is a mass average molecular weight in terms of polystyrene, which can be measured by the gel permeation chromatography based on polystyrene.

[0025] The polysiloxane can be used alone or in combination of two or more of any of these. The content of the polysiloxane is preferably 2.0 to 40.0 mass %, more preferably 3.0 to 30.0 mass %, based on the total mass of the polysiloxane composition.

[0026] Such a polysiloxane can be obtained by hydrolysis and condensation of, for example, a silicon compound represented by the formula (ia) and/or a silicon compound represented by the formula (ib), if necessary, in the presence of an acidic catalyst or a basic catalyst:



wherein

P is an integer of 1 to 3;

R^{1'} is hydrogen, a mono- to trivalent, linear, branched or cyclic, saturated or unsaturated, C₁₋₃₀ aliphatic

- hydrocarbon group, or a mono- to trivalent, C₆₋₃₀ aromatic hydrocarbon group;
 the aliphatic hydrocarbon group and the aromatic hydrocarbon group are each unsubstituted or substituted
 5 with fluorine, hydroxy or C₁₋₈ alkoxy;
 in the aliphatic hydrocarbon group and the aromatic hydrocarbon group, methylene is not replaced, or one or more methylene are replaced with oxy, imide or carbonyl, provided that R^{1'} is neither hydroxy nor
 10 alkoxy; and
 R^a is C₁₋₁₀ alkyl, preferably methyl, ethyl, n-propyl, isopropyl and n-butyl, and

$$\text{Si}(\text{OR}^b)_4 \quad (\text{ib})$$

 wherein
 15 R^b is C₁₋₁₀ alkyl, preferably methyl, ethyl, n-propyl, isopropyl and n-butyl.
- [0027] Exemplified embodiments of the silicon compound represented by the general formula (ia) include
 20 methyltrimethoxysilane, methyltriethoxysilane, methyltriisopropoxysilane, methyltri-n-butoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethyltriisopropoxysilane, ethyltri-n-butoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, n-butyltrimethoxysilane, n-butyltriethoxysilane, n-
 25 hexyltrimethoxysilane, n-hexyltriethoxysilane, decyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, trifluoromethyltrimethoxysilane, trifluoromethyltriethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, tris-(3-trimethoxysilylpropyl)isocyanurate, tris- (3-
 30 triethoxysilylpropyl)isocyanurate and tris- (3-trimethoxysilylethyl)isocyanurate, and among them, methyltrimethoxysilane, methyltriethoxysilane, methyltripropoxysilane and phenyltrimethoxysilane are preferred.
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- [0028] Exemplified embodiments of the silicon compound

represented by the general formula (ib) include tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetra-iso-propoxysilane, tetra-n-butoxysilane, tetra-sec-butoxysilane, tetra-tert-butoxysilane and tetrakis(2-ethylbutoxy) silane, and among them, tetramethoxysilane, tetraethoxysilane and tetra-iso-propoxysilane are preferred.

[0029] Here, the silicon compounds can be used in combination of two or more of any of these.

10 [0030] (II) Ionic liquid

The composition according to the present invention comprises an ionic liquid.

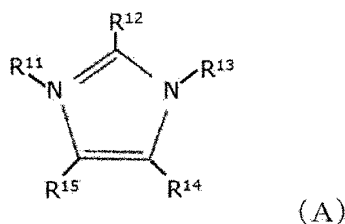
15 The ionic liquid is a salt that exists as a liquid in a wide temperature range, and is a liquid consisting only of ions. Generally, a salt having a melting point of 100°C or lower is defined as an ionic liquid. The ionic liquid used in the present invention has a melting point of 100°C or lower, preferably 80°C or lower, more preferably 60°C or lower, further preferably 30°C or lower.

20 The ionic liquid used in the present invention is preferably a basic ionic liquid, preferably one composed of a combination of a strong base and a weak acid.

[0031] The cation of the ionic liquid is preferably at least one cation selected from the group consisting of an imidazolium type ion, a pyrrolidinium type ion, a piperidinium type ion, a pyridinium type ion, and an ammonium type ion, and more preferably an imidazolium type ion.

30 [0032] The imidazolium type ion is preferably represented by the following formula (A):

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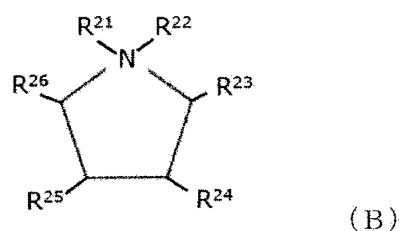
wherein

R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ are each independently hydrogen, linear or branched, C₁₋₁₈ alkyl, cyclic C₅₋₁₂ alkyl or C₆₋₁₄ aryl.

[0033] Exemplified embodiments of the imidazolium type ion include 1-methylimidazolium, 1-methyl-2-ethylimidazolium, 1-methyl-3-octylimidazolium, 1,2-dimethylimidazolium, 1,3-dimethylimidazolium, 2,3-dimethylimidazolium, 3,4-dimethylimidazolium, 1,2,3-trimethylimidazolium, 1,3,4-trimethylimidazolium, 1,3,4,5-tetramethylimidazolium, 1-ethylimidazolium, 1-ethyl-2-methyl imidazolium, 1-ethyl-3-methylimidazolium, 1-ethyl-2,3-dimethylimidazolium, 2-ethyl-3,4-dimethylimidazolium, 1-propyl imidazolium, 1-propyl-2-methyl imidazolium, 1-propyl-3-methylimidazolium, 1-propyl-2,3-dimethylimidazolium, 1,3-dipropylimidazolium, 1-butyliimidazolium, 1-butyl-2-methylimidazolium, 1-butyl-3-methylimidazolium, 1-butyl-4-methylimidazolium, 1-butyl-2,3-dimethylimidazolium, 1-butyl-3,4-dimethylimidazolium, 1-butyl-3,4,5-trimethylimidazolium, 1-butyl-2-ethylimidazolium, 1-butyl-3-ethylimidazolium, 1-butyl-2-ethyl-5-methylimidazolium, 1,3-dibutyliimidazolium, 1,3-dibutyl-2-methylimidazolium, 1-pentyliimidazolium, 1-pentyl-2-methylimidazolium, 1-pentyl-3-methylimidazolium, 1-pentyl-2,3-dimethylimidazolium, 1-hexylimidazolium, 1-hexyl-2-methylimidazolium, 1-hexyl-3-methylimidazolium, 1-hexyl-2,3-dimethylimidazolium, 1-octyl-2-methylimidazolium, 1-octyl-3-methylimidazolium, 1-decyl-3-

methylimidazolium, 1-dodecyl-3-methylimidazolium, 1-tetradecyl-3-methylimidazolium, 1-hexadecyl-3-methylimidazolium and 1-benzyl-3-methylimidazolium, and preferably 1-ethyl-3-methylimidazolium, 1-ethyl-2,3-dimethylimidazolium, 1,3-dimethylimidazolium, 1,2,3-trimethylimidazolium, 1-propyl-3-methylimidazolium, 1-propyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium, 1-butyl-2,3-dimethylimidazolium and 1-octyl-3-methylimidazolium.

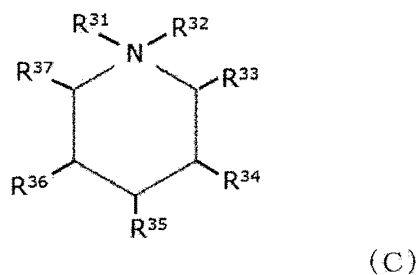
[0034] The pyrrolidinium type ion is preferably represented by the following formula (B):



wherein
 R^{21} , R^{22} , R^{23} , R^{24} , R^{25} and R^{26} are each independently hydrogen, linear or branched, C_{1-18} alkyl, cyclic C_{5-12} alkyl, or C_{6-14} aryl.

[0035] Exemplified embodiments of the pyrrolidinium type ion include 1-methyl-1-ethylpyrrolidinium, 1-methyl-1-propylpyrrolidinium, 1-methyl-1-butylpyrrolidinium, 1-methyl-1-pentylpyrrolidinium, 1-methyl-1-hexylpyrrolidinium and 1-methyl-1-octylpyrrolidinium, and preferably 1-methyl-1-propylpyrrolidinium.

[0036] The piperidinium type ion is preferably represented by the following formula (C):



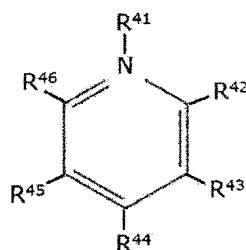
wherein

R^{31} , R^{32} , R^{33} , R^{34} , R^{35} , R^{36} and R^{37} are each independently hydrogen, linear or branched C_{1-18} alkyl, cyclic C_{5-12} alkyl, or C_{6-14} aryl.

5 [0037] Exemplified embodiments of the piperidinium type ion include 1-methyl-1-ethylpiperidinium, 1-methyl-1-propylpiperidinium, 1-methyl-1-butylpiperidinium, 1-methyl-1-pentylpiperidinium, 1-methyl-1-hexylpiperidinium and 1-methyl-1-octylpiperidinium, and preferably 1-methyl-1-butylpiperidinium.

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[0038] The pyridinium type ion is preferably represented by the following formula (D):



(D)

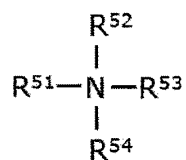
wherein

15 R^{41} , R^{42} , R^{43} , R^{44} , R^{45} and R^{46} are each independently hydrogen, linear or branched, C_{1-18} alkyl, cyclic C_{5-12} alkyl, or C_{6-14} aryl.

[0039] Exemplified embodiments of the pyridinium type ion include 1-methylpyridinium, 1-ethylpyridinium, 1-propylpyridinium, 1-butylpyridinium, 1-pentylpyridinium, 1-hexylpyridinium, 1-octylpyridinium, 1-methyl-3-ethylpyridinium, 1-methyl-4-ethylpyridinium, 1-methyl-3-butylpyridinium, 1-methyl-4-butylpyridinium, 1-ethyl-3-methylpyridinium, 1-ethyl-4-methylpyridinium, 1-propyl-3-methylpyridinium, 1-propyl-4-methylpyridinium, 1-butyl-3-methylpyridinium, 1-butyl-4-methylpyridinium, 1-hexyl-4-methylpyridinium and 1-octyl-4-methylpyridinium, and preferably 1-butylpyridinium and 1-ethyl-4-methylpyridinium.

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[0040] The ammonium type ion is preferably represented by the following formula (E):



(E)

wherein

5 R^{51} , R^{52} , R^{53} and R^{54} are each independently linear or branched, C_{1-18} alkyl, linear or branched, C_{1-18} hydroxyalkyl, cyclic C_{5-12} alkyl, or C_{6-14} aryl.

[0041] Exemplified embodiments of the ammonium type ion include trimethylethylammonium,
10 trimethylbutylammonium, triethylmethylammonium, tripropylmethylammonium, tributylmethylammonium, trihexylmethylammonium, trioctylmethylammonium, tetrabutylammonium, 2-hydroxyethyltrimethylammonium and tris(2-hydroxyethyl)methylammonium, and preferably
15 tetrabutylammonium, tributylmethylammonium and 2-hydroxyethyltrimethylammonium.

[0042] The anion of the ionic liquid is preferably at least one anion selected from the group consisting of a
20 formate ion, an acetate ion, a propionate ion, a lactate ion, an oleate ion, a salicylate ion, a dicyanamide ion, a cyanamide ion, a thiocyanate ion, a methyl sulfate ion, an ethyl sulfate ion, a hydrogen sulfate ion, a methane sulfonate ion, a trifluoromethane sulfonate ion, a p-toluene sulfonate ion, a bis(trifluoromethylsulfonyl)imide
25 ion, a bis(fluorosulfonyl)imide ion, a methyl carbonate ion, a hydrogen carbonate ion, a diethyl phosphate ion, a dibutyl phosphate ion, a hexafluorophosphate ion, a tetrafluoroborate ion, a chlorine ion and a bromine ion,
30 and more preferably an acetate ion, a dicyanamide ion, a cyanamide ion, a chlorine ion and a bromine ion.

[0043] In a preferred embodiment, exemplified
embodiments of the ionic liquid include
trimethylbutylammonium
bis(trifluoromethylsulfonyl)imide,
5 tributylmethylammonium dicyanamide,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide, tris(2-
hydroxyethyl)methylammonium methylsulfate, 2-
hydroxyethyltrimethylammonium acetate, 2-
10 hydroxyethyltrimethylammonium lactate, 2-
hydroxyethyltrimethylammonium salicylate,
tetrabutylammonium chloride, 1,3-dimethylimidazolium
methylsulfate, 1,2,3-trimethylimidazolium methylsulfate,
1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-
15 methylimidazolium dicyanamide, 1-ethyl-3-
methylimidazolium methylsulfate, 1-ethyl-3-
methylimidazolium thiocyanate, 1-ethyl-2,3-
dimethylimidazolium bis(trifluoromethylsulfonyl)imide,
1-propyl-3-methylimidazolium acetate, 1-propyl-3-
20 methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-
propyl-2,3-dimethylimidazolium
bis(trifluoromethylsulfonyl)imide, 1-butyl-3-
methylimidazolium acetate, 1-butyl-3-methylimidazolium
dicyanamide, 1-butyl-3-methylimidazolium thiocyanate,
25 1-butyl-3-methylimidazolium bromide, 1-butyl-3-
methylimidazolium hexafluorophosphate, 1-butyl-3-
methylimidazolium tetrafluoroborate, 1-butyl-2,3-
dimethylimidazolium bis(trifluoromethylsulfonyl)imide,
1-octyl-3-methylimidazolium acetate, 1-octyl-3-
30 methylimidazolium bromide, 1-octyl-3-
methylimidazolium tetrafluoroborate, 1-methyl-1-
butylpyrrolidinium dicyanamide, 1-methyl-1-
octylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 1-
methyl-1-butylpiperidinium
35 bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-
methylpyridinium ethylsulfate, 1-butyl-4-

methyipyridinium bis(trifluoromethylsulfonyl)imide and 1-butylpyridinium tetrafluoroborate. In a more preferred embodiment, the ionic liquid has an imidazolium type ion as a cation and an acetate as an anion, and exemplified embodiments thereof include 1-ethyl-3-methylimidazolium acetate, 1-propyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium acetate and 1-octyl-3-methylimidazolium acetate.

[0044] The ionic liquid has catalytic action that promotes the curing of polysiloxane, and it is assumed that the curing can be completed even at a relatively low temperature.

The compounding ratio of the ionic liquid to the polysiloxane (ionic liquid / polysiloxane) is preferably 0.000030 to 0.10, more preferably 0.000050 to 0.10, and further preferably 0.00010 to 0.10 in terms of mass ratio. This is because, due to being in such a range, the effect of low temperature curing is more exhibited and the density of the cured film tends to be increased.

Further, since the ionic liquid can be uniformly present in the composition as compared with the commonly used curing accelerator (for example, a thermal base generator), it is assumed that the ionic liquid exhibits effects on suppressing voids.

[0045] The ionic liquid can be used alone or in combination of two or more of any of these. The content of the ionic liquid is preferably 0.00020 to 4.0 mass %, more preferably 0.00020 to 3.2 mass %, based on the total mass of the composition according to the present invention.

[0046] (III) Acid

The composition according to the present invention comprises an acid.

The acid may be an inorganic acid or an organic acid, but is preferably an organic acid, more preferably a carboxylic acid, further preferably a monocarboxylic acid

or a dicarboxylic acid, further more preferably a dicarboxylic acid.

[0047] Examples of the monocarboxylic acid include acetic acid, formic acid, propionic acid, butyric acid, valeric acid and acrylic acid, and acetic acid is preferable.

5 Examples of the dicarboxylic acid include oxalic acid, maleic acid, fumaric acid, phthalic acid, succinic acid, glutaconic acid, aspartic acid, glutamic acid, malic acid, citraconic acid, acetylenedicarboxylic acid, itaconic acid, mesaconic acid, 3-aminohexandioic acid and malonic acid, preferably oxalic acid, maleic acid, fumaric acid, phthalic acid, succinic acid, malic acid, citraconic acid, acetylenedicarboxylic acid or malonic acid, more preferably oxalic acid, maleic acid, fumaric acid, phthalic acid, citraconic acid or acetylenedicarboxylic acid.

15 [0048] It is preferable that the acid has high sublimability, which is to sublime when heated for curing. In particular, the sublimation temperature is preferably 90 to 300°C, more preferably 90 to 250°C. This is because the residual amount of the cured film is reduced by the sublimation of the acid when the coating film is cured.

20 [0049] Although not wishing to be bound by theory, as described above, the ionic liquid functions as a catalyst that accelerates the curing of polysiloxane at a low temperature. With respect to the composition comprising an ionic liquid, a polysiloxane and a solvent, there is a case that curing is proceeded even during long-term storage at room temperature, resulting in gelation or the like. On the other hand, it is assumed that by combining an acid, it is possible to suppress the catalytic action of the ionic liquid and exhibit good storage stability. It is assumed that the sublimation of the acid during heating for curing makes the catalytic action of the ionic liquid be exhibited and cure at a low temperature. In order to exhibit better storage stability and low temperature curability, the present invention

preferably comprises a combination of an ionic liquid and a carboxylic acid, more preferably a combination of an ionic liquid and oxalic acid, maleic acid, fumaric acid, phthalic acid, citraconic acid or acetylenedicarboxylic acid, further preferably a combination of an ionic liquid in which the cation is an imidazolium type ion and the anion is an acetate ion, and maleic acid.

[0050] In a preferred embodiment, exemplified embodiments of the combination of the ionic liquid and the acid (ionic liquid / acid) include tributylmethylammonium dicyanamide / acetic acid, tris(2-hydroxyethyl)methylammonium methylsulfate / acetic acid, 2-hydroxyethyltrimethylammonium acetate / acetic acid, 2-hydroxyethyltrimethylammonium lactate / acetic acid, 2-hydroxyethyltrimethylammonium salicylate / acetic acid, tetrabutylammonium chloride / acetic acid, 1-ethyl-3-methylimidazolium acetate / acetic acid, 1-ethyl-3-methylimidazolium dicyanamide / acetic acid, 1-ethyl-3-methylimidazolium methylsulfate / acetic acid, 1-ethyl-3-methylimidazolium thiocyanate / acetic acid, 1-propyl-3-methylimidazolium acetate / acetic acid, 1-butyl-3-methylimidazolium acetate / acetic acid, 1-butyl-3-methylimidazolium dicyanamide / acetic acid, 1-butyl-3-methylimidazolium thiocyanate / acetic acid, 1-butyl-3-methylimidazolium bromide / acetic acid, 1-octyl-3-methylimidazolium acetate / acetic acid, 1-octyl-3-methylimidazolium bromide / acetic acid, tributylmethylammonium dicyanamide / succinic acid, tris(2-hydroxyethyl)methylammonium methylsulfate / succinic acid, 2-hydroxyethyltrimethylammonium acetate / succinic acid, 2-hydroxyethyltrimethylammonium lactate / succinic acid, 2-hydroxyethyltrimethylammonium salicylate / succinic acid, tetrabutylammonium chloride / succinic acid, 1-ethyl-3-methylimidazolium acetate / succinic acid, 1-ethyl-3-methylimidazolium dicyanamide / succinic acid,

- 1-ethyl-3-methylimidazolium methylsulfate / succinic acid, 1-ethyl-3-methylimidazolium thiocyanate / succinic acid, 1-propyl-3-methylimidazolium acetate / succinic acid, 1-butyl-3-methylimidazolium acetate / succinic acid, 1-butyl-3-methylimidazolium dicyanamide / succinic acid, 1-butyl-3-methylimidazolium thiocyanate / succinic acid, 1-butyl-3-methylimidazolium bromide / succinic acid, 1-octyl-3-methylimidazolium acetate / succinic acid, 1-octyl-3-methylimidazolium bromide / succinic acid, 1-methyl-1-butylpyrrolidinium dicyanamide / succinic acid, tributylmethylammonium dicyanamide / glutaconic acid, tris(2-hydroxy)ethyl)methylammonium methylsulfate / glutaconic acid, 2-hydroxyethyltrimethylammonium acetate / glutaconic acid, 2-hydroxyethyltrimethylammonium lactate / glutaconic acid, 2-hydroxyethyltrimethylammonium salicylate / glutaconic acid, tetrabutylammonium chloride / glutaconic acid, 1-ethyl-3-methylimidazolium acetate / glutaconic acid, 1-ethyl-3-methylimidazolium dicyanamide / glutaconic acid, 1-ethyl-3-methylimidazolium methylsulfate / glutaconic acid, 1-ethyl-3-methylimidazolium thiocyanate / glutaconic acid, 1-propyl-3-methylimidazolium acetate / glutaconic acid, 1-butyl-3-methylimidazolium acetate / glutaconic acid, 1-butyl-3-methylimidazolium dicyanamide / glutaconic acid, 1-butyl-3-methylimidazolium thiocyanate / glutaconic acid, 1-butyl-3-methylimidazolium bromide / glutaconic acid, 1-octyl-3-methylimidazolium acetate / glutaconic acid, 1-octyl-3-methylimidazolium bromide / glutaconic acid, trimethylbutylammonium bis(trifluoromethylsulfonyl)imide / citraconic acid, tributylmethylammonium dicyanamide / citraconic acid, tributylmethylammonium bis(trifluoromethylsulfonyl)imide / citraconic acid, tris(2-hydroxyethyl)methylammonium methylsulfate / citraconic acid, 2-hydroxyethyltrimethylammonium

- acetate / citraconic acid, 2-hydroxyethyltrimethylammonium lactate / citraconic acid, 2-hydroxyethyltrimethylammonium salicylate / citraconic acid, tetrabutylammonium chloride / citraconic acid, 1,3-dimethylimidazolium methylsulfate / citraconic acid, 1,2,3-trimethylimidazolium methylsulfate / citraconic acid, 1-ethyl-3-methylimidazolium acetate / citraconic acid, 1-ethyl-3-methylimidazolium dicyanamide / citraconic acid, 1-ethyl-3-methylimidazolium methylsulfate / citraconic acid, 1-ethyl-3-methylimidazolium thiocyanate / citraconic acid, 1-propyl-3-methylimidazolium acetate / citraconic acid, 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-butyl-3-methylimidazolium acetate / citraconic acid, 1-butyl-3-methylimidazolium dicyanamide / citraconic acid, 1-butyl-3-methylimidazolium thiocyanate / citraconic acid, 1-butyl-3-methylimidazolium bromide / citraconic acid, 1-butyl-3-methylimidazolium hexafluorophosphate / citraconic acid, 1-butyl-3-methylimidazolium tetrafluoroborate / citraconic acid, 1-octyl-3-methylimidazolium acetate / citraconic acid, 1-octyl-3-methylimidazolium bromide / citraconic acid, 1-octyl-3-methylimidazolium tetrafluoroborate / citraconic acid, 1-methyl-1-butylpyrrolidinium dicyanamide / citraconic acid, 1-methyl-1-octylpyrrolidinium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-methyl-1-butylpiperidinium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-ethyl-3-methylpyridinium ethylsulfate / citraconic acid, 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-butylpyridinium tetrafluoroborate / citraconic acid, trimethylbutylammonium bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic acid, tributylmethylammonium dicyanamide /

acetylenedicarboxylic acid, tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, tris(2-hydroxyethyl)methylammonium
methylsulfate / acetylenedicarboxylic acid, 2-
5 hydroxyethyltrimethylammonium acetate /
acetylenedicarboxylic acid, 2-
hydroxyethyltrimethylammonium lactate /
acetylenedicarboxylic acid, 2-
hydroxyethyltrimethylammonium salicylate /
10 acetylenedicarboxylic acid, tetrabutylammonium chloride
/ acetylenedicarboxylic acid, 1,3-dimethylimidazolium
methylsulfate / acetylenedicarboxylic acid, 1,2,3-
trimethylimidazolium methylsulfate /
acetylenedicarboxylic acid, 1-ethyl-3-methylimidazolium
15 acetate / acetylenedicarboxylic acid, 1-ethyl-3-
methylimidazolium dicyanamide / acetylenedicarboxylic
acid, 1-ethyl-3-methylimidazolium methylsulfate /
acetylenedicarboxylic acid, 1-ethyl-3-methylimidazolium
thiocyanate / acetylenedicarboxylic acid, 1-propyl-3-
20 methylimidazolium acetate / acetylenedicarboxylic acid,
1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, 1-butyl-3-methylimidazolium acetate /
acetylenedicarboxylic acid, 1-butyl-3-methylimidazolium
25 dicyanamide / acetylenedicarboxylic acid, 1-butyl-3-
methylimidazolium thiocyanate / acetylenedicarboxylic
acid, 1-butyl-3-methylimidazolium bromide /
acetylenedicarboxylic acid, 1-butyl-3-methylimidazolium
hexafluorophosphate / acetylenedicarboxylic acid, 1-
30 butyl-3-methylimidazolium tetrafluoroborate /
acetylenedicarboxylic acid, 1-octyl-3-methylimidazolium
acetate / acetylenedicarboxylic acid, 1-octyl-3-
methylimidazolium bromide / acetylenedicarboxylic acid,
1-octyl-3-methylimidazolium tetrafluoroborate /
35 acetylenedicarboxylic acid, 1-methyl-1-
butylpyrrolidinium dicyanamide / acetylenedicarboxylic

- acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, 1-methyl-1-butylpiperidinium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
5 acid, 1-ethyl-3-methylpyridinium ethylsulfate /
acetylenedicarboxylic acid, 1-butyl-4-methylpyridinium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, 1-butylpyridinium tetrafluoroborate /
acetylenedicarboxylic acid, trimethylbutylammonium
10 bis(trifluoromethylsulfonyl)imide / oxalic acid,
tributylmethylammonium dicyanamide / oxalic acid ,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / oxalic acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / oxalic
15 acid, 2-hydroxyethyltrimethylammonium acetate / oxalic
acid, 2-hydroxyethyltrimethylammonium lactate / oxalic
acid, 2-hydroxyethyltrimethylammonium salicylate /
oxalic acid, tetrabutylammonium chloride / oxalic acid,
1,3-dimethylimidazolium methylsulfate / oxalic acid,
20 1,2,3-trimethylimidazolium methylsulfate / oxalic acid,
1-ethyl-3-methylimidazolium acetate / oxalic acid, 1-
ethyl-3-methylimidazolium dicyanamide / oxalic acid, 1-
ethyl-3-methylimidazolium methylsulfate / oxalic acid,
1-ethyl-3- methylimidazolium thiocyanate / oxalic acid,
25 1-propyl-3-methylimidazolium acetate / oxalic acid, 1-
propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / oxalic acid, 1-butyl-3-
methylimidazolium acetate / oxalic acid, 1-butyl-3-
methylimidazolium dicyanamide / oxalic acid, 1-butyl-3-
30 methylimidazolium thiocyanate / oxalic acid, 1-butyl-3-
methylimidazolium bromide / oxalic acid, 1-butyl-3-
methylimidazolium hexafluorophosphate / oxalic acid, 1-
butyl-3-methylimidazolium tetrafluoroborate / oxalic
acid, 1-octyl-3-methylimidazolium acetate / oxalic acid,
35 1-octyl-3-methylimidazolium bromide / oxalic acid, 1-
octyl-3-methylimidazolium tetrafluoroborate / oxalic

- acid, 1-methyl-1-butylpyrrolidinium dicyanamide / oxalic acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / oxalic acid, 1-methyl-1-butylpiperidinium bis(trifluoromethylsulfonyl)imide /
5 oxalic acid, 1-ethyl-3-methylpyridinium ethylsulfate /
oxalic acid, 1-butyl-4-methylpyridinium
bis(trifluoromethylsulfonyl)imide / oxalic acid, 1-
butylpyridinium tetrafluoroborate / oxalic acid,
trimethylbutylammonium
10 bis(trifluoromethylsulfonyl)imide / maleic acid,
tributylmethylammonium dicyanamide / maleic acid,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / maleic acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / maleic
15 acid, 2-hydroxyethyltrimethylammonium acetate /
maleic acid, 2-hydroxyethyltrimethylammonium lactate /
maleic acid, 2-hydroxyethyltrimethylammonium
salicylate / maleic acid, tetrabutylammonium chloride /
maleic acid, 1,3-dimethylimidazolium methylsulfate /
20 maleic acid, 1,2,3-trimethylimidazolium methylsulfate /
maleic acid, 1-ethyl-3-methylimidazolium acetate /
maleic acid, 1-ethyl-3-methylimidazolium dicyanamide /
maleic acid, 1-ethyl-3-methylimidazolium methylsulfate
/ maleic acid, 1-ethyl-3-methylimidazolium thiocyanate /
25 maleic acid, 1-propyl-3-methylimidazolium acetate /
maleic acid, 1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / maleic acid, 1-butyl-
3-methylimidazolium acetate / maleic acid, 1-butyl-3-
methylimidazolium dicyanamide / maleic acid, 1-butyl-3-
30 methylimidazolium thiocyanate / maleic acid, 1-butyl-3-
methylimidazolium bromide / maleic acid, 1-butyl-3-
methylimidazolium hexafluorophosphate / maleic acid,
1-butyl-3-methylimidazolium tetrafluoroborate / maleic
acid, 1-octyl-3-methylimidazolium acetate / maleic acid,
35 1-octyl-3-methylimidazolium bromide / maleic acid, 1-
octyl-3-methylimidazolium tetrafluoroborate / maleic

- acid, 1-methyl-1-butylpyrrolidinium dicyanamide /
maleic acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / maleic acid, 1-
methyl-1-butylpiperidinium
- 5 bis(trifluoromethylsulfonyl)imide / maleic acid, 1-ethyl-
3-methylpyridinium ethylsulfate / maleic acid, 1-butyl-4-
methylpyridinium bis(trifluoromethylsulfonyl)imide /
maleic acid, 1-butylpyridinium tetrafluoroborate / maleic
acid, trimethylbutylammonium
- 10 bis(trifluoromethylsulfonyl)imide / fumaric acid,
tributylmethylammonium dicyanamide / fumaric acid,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / fumaric acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / fumaric
acid, 2-hydroxyethyltrimethylammonium acetate /
- 15 fumaric acid, 2-hydroxyethyltrimethylammonium lactate
/ fumaric acid, 2-hydroxyethyltrimethylammonium
salicylate / fumaric acid, tetrabutylammonium chloride /
fumaric acid, 1,3-dimethylimidazolium methylsulfate /
- 20 fumaric acid, 1,2,3-trimethylimidazolium methylsulfate /
fumarate, 1-ethyl-3-methylimidazolium acetate / fumaric
acid, 1-ethyl-3-methylimidazolium dicyanamide / fumaric
acid, 1-ethyl-3-methylimidazolium methylsulfate /
- 25 fumaric acid, 1-ethyl-3-methylimidazolium thiocyanate /
fumaric acid, 1-propyl-3-methylimidazolium acetate /
fumaric acid, 1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-butyl-
3-methylimidazolium acetate / fumaric acid, 1-butyl-3-
methylimidazolium dicyanamide / fumaric acid, 1-butyl-
3-methylimidazolium thiocyanate / fumaric acid, 1-butyl-3-
methylimidazolium bromide / fumaric acid, 1-butyl-3-
methylimidazolium hexafluorophosphate / fumaric acid,
1-butyl-3-methylimidazolium tetrafluoroborate / fumaric
acid, 1-octyl-3-methylimidazolium acetate / fumaric
- 35 acid, 1-octyl-3-methylimidazolium bromide / fumaric
acid, 1-octyl-3-methylimidazolium tetrafluoroborate /

- fumaric acid, 1-methyl-1-butylpyrrolidinium dicyanamide / fumaric acid, 1-methyl-1-octylpyrrolidinium bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-methyl-1-butylpiperidinium
- 5 bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-ethyl-3-methylpyridinium ethylsulfate / fumaric acid, 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-butylpyridinium tetrafluoroborate / fumaric acid, trimethylbutylammonium
- 10 bis(trifluoromethylsulfonyl)imide / phthalic acid, tributylmethylammonium dicyanamide / phthalic acid, tributylmethylammonium bis(trifluoromethylsulfonyl)imide / phthalic acid, tris(2-hydroxyethyl)methylammonium methylsulfate / phthalic acid, 2-hydroxyethyltrimethylammonium acetate /
- 15 phthalic acid, 2-hydroxyethyltrimethylammonium lactate / phthalic acid, 2-hydroxyethyltrimethylammonium salicylate / phthalic acid, tetrabutylammonium chloride / phthalic acid, 1,3-dimethylimidazolium methylsulfate /
- 20 phthalic acid, 1,2,3-trimethylimidazolium methylsulfate / phthalic acid, 1-ethyl-3-methylimidazolium acetate / phthalic acid, 1-ethyl-3-methylimidazolium dicyanamide / phthalic acid, 1-ethyl-3-methylimidazolium methylsulfate / phthalic acid, 1-ethyl-3-
- 25 methylimidazolium thiocyanate / phthalic acid, 1-propyl-3-methylimidazolium acetate / phthalic acid, 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide / phthalic acid, 1-butyl-3-methylimidazolium acetate / phthalic acid, 1-butyl-3-methylimidazolium dicyanamide
- 30 / phthalic acid, 1-butyl-3-methylimidazolium thiocyanate / phthalic acid, 1-butyl-3-methylimidazolium bromide / phthalic acid, 1-butyl-3-methylimidazolium hexafluorophosphate / phthalic acid, 1-butyl-3-
- 35 methylimidazolium tetrafluoroborate / phthalic acid, 1-octyl-3-methylimidazolium acetate / phthalic acid, 1-octyl-3-methylimidazolium bromide / phthalic acid, 1-

octyl-3-methyl imidazolium tetrafluoroborate / phthalic acid, 1-methyl-1-butylpyrrolidinium dicyanamide / phthalic acid, 1-methyl-1-octylpyrrolidinium bis(trifluoromethylsulfonyl)imide / phthalic acid, 1-methyl-1-butylpiperidinium bis(trifluoromethylsulfonyl)imide / phthalic acid, 1-ethyl-3-methylpyridinium ethylsulfate / phthalic acid, 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide / phthalic acid, and 1-butylpyridinium tetrafluoroborate / phthalic acid.

[0051] In a more preferred embodiment, exemplified embodiments of the combination of the ionic liquid and the acid (ionic liquid / acid) include trimethylbutylammonium bis(trifluoromethylsulfonyl)imide / citraconic acid, tributylmethylammonium dicyanamide / citraconic acid, tributylmethylammonium bis(trifluoromethylsulfonyl)imide / citraconic acid, tris(2-hydroxyethyl)methylammonium methylsulfate / citraconic acid, 2-hydroxyethyltrimethylammonium acetate / citraconic acid, 2-hydroxyethyltrimethylammonium lactate / citraconic acid, 2-hydroxyethyltrimethylammonium salicylate / citraconic acid, tetrabutylammonium chloride / citraconic acid, 1,3-dimethylimidazolium methylsulfate / citraconic acid, 1,2,3-trimethylimidazolium methylsulfate / citraconic acid, 1-ethyl-3-methylimidazolium acetate / citraconic acid, 1-ethyl-3-methylimidazolium dicyanamide / citraconic acid, 1-ethyl-3-methylimidazolium methylsulfate / citraconic acid, 1-ethyl-3-methylimidazolium thiocyanate / citraconic acid, 1-propyl-3-methylimidazolium acetate / citraconic acid, 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-butyl-3-methylimidazolium acetate / citraconic acid, 1-butyl-3-methylimidazolium dicyanamide / citraconic acid,

- 1-butyl-3-methylimidazolium thiocyanate / citraconic acid, 1-butyl-3-methylimidazolium bromide / citraconic acid, 1-butyl-3-methylimidazolium hexafluorophosphate / citraconic acid, 1-butyl-3-methylimidazolium
- 5 tetrafluoroborate / citraconic acid, 1-octyl-3-methylimidazolium acetate / citraconic acid, 1-octyl-3-methylimidazolium bromide / citraconic acid, 1-octyl-3-methylimidazolium tetrafluoroborate / citraconic acid, 1-methyl-1-butylpyrrolidinium dicyanamide / citraconic
- 10 acid, 1-methyl-1-octylpyrrolidinium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-methyl-1-butylpiperidinium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-ethyl-3-methylpyridinium ethylsulfate / citraconic acid,
- 15 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide / citraconic acid, 1-butylpyridinium tetrafluoroborate / citraconic acid, trimethylbutylammonium bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
- 20 acid, tributylmethylammonium dicyanamide / acetylenedicarboxylic acid, tributylmethylammonium bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic acid, tris(2-hydroxyethyl)methylammonium
- 25 methylsulfate / acetylenedicarboxylic acid, 2-hydroxyethyltrimethylammonium acetate / acetylenedicarboxylic acid, 2-hydroxyethyltrimethylammonium lactate / acetylenedicarboxylic acid, 2-hydroxyethyltrimethylammonium salicylate / acetylene
- 30 dicarboxylic acid, tetrabutylammonium chloride / acetylenedicarboxylic acid, 1,3-dimethylimidazolium methylsulfate / acetylenedicarboxylic acid, 1,2,3-trimethylimidazolium methylsulfate / acetylenedicarboxylic acid, 1-ethyl-3-methylimidazolium
- 35 acetate / acetylenedicarboxylic acid, 1-ethyl-3-methylimidazolium dicyanamide / acetylenedicarboxylic

acid, 1-ethyl-3-methylimidazolium methylsulfate /
acetylenedicarboxylic acid, 1-ethyl-3-methylimidazolium
thiocyanate / acetylene dicarboxylic acid, 1-propyl-3-
methylimidazolium acetate / acetylenedicarboxylic acid,
5 1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, 1-butyl-3-methylimidazolium acetate /
acetylenedicarboxylic acid, 1-butyl-3-methylimidazolium
dicyanamide / acetylenedicarboxylic acid, 1-butyl-3-
10 methylimidazolium thiocyanate / acetylenedicarboxylic
acid, 1-butyl-3-methylimidazolium bromide /
acetylenedicarboxylic acid, 1-butyl-3-methylimidazolium
hexafluorophosphate / acetylenedicarboxylic acid, 1-
butyl-3-methylimidazolium tetrafluoroborate /
15 acetylenedicarboxylic acid, 1-octyl-3-methylimidazolium
acetate / acetylenedicarboxylic acid, 1-octyl-3-
methylimidazolium bromide / acetylenedicarboxylic acid,
1-octyl-3-methylimidazolium tetrafluoroborate /
acetylenedicarboxylic acid, 1-methyl-1-
20 butylpyrrolidinium dicyanamide / acetylenedicarboxylic
acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, 1-methyl-1-butylpiperidinium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
25 acid, 1-ethyl-3-methylpyridinium ethylsulfate /
acetylenedicarboxylic acid, 1-butyl-4-methylpyridinium
bis(trifluoromethylsulfonyl)imide / acetylenedicarboxylic
acid, 1-butylpyridinium tetrafluoroborate /
acetylenedicarboxylic acid, trimethylbutylammonium
30 bis(trifluoromethylsulfonyl)imide / oxalic acid,
tributylmethylammonium dicyanamide / oxalic acid,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / oxalic acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / oxalic
35 acid, 2-hydroxyethyltrimethylammonium acetate / oxalic
acid, 2-hydroxyethyltrimethylammonium lactate / oxalic

- acid, 2-hydroxyethyltrimethylammonium salicylate /
carboxylic acid, tetrabutylammonium chloride / oxalic
acid, 1,3-dimethylimidazolium methylsulfate / oxalic
acid, 1,2,3-trimethylimidazolium methylsulfate / oxalic
5 acid, 1-ethyl-3-methylimidazolium acetate / oxalic acid,
1-ethyl-3-methylimidazolium dicyanamide / oxalic acid,
1-ethyl-3-methylimidazolium methyl sulfate / oxalic
acid, 1-ethyl-3-methylimidazolium thiocyanate / oxalic
acid, 1-propyl-3-methylimidazolium acetate / oxalic acid,
10 1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / oxalic acid, 1-butyl-3-
methylimidazolium acetate / oxalic acid, 1-butyl-3-
methylimidazolium dicyanamide / oxalic acid, 1-butyl-3-
methylimidazolium thiocyanate / oxalic acid, 1-butyl-3 -
15 methylimidazolium bromide / oxalic acid, 1-butyl-3-
methylimidazolium hexafluorophosphate / oxalic acid, 1-
butyl-3-methylimidazolium tetrafluoroborate / oxalic
acid, 1-octyl-3-methylimidazolium acetate / oxalic acid,
1-octyl-3-methylimidazolium bromide / oxalic acid, 1-
20 octyl-3-methylimidazolium tetrafluoroborate / oxalic
acid, 1-methyl-1-butylpyrrolidinium dicyanamide / oxalic
acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / oxalic acid, 1-methyl-
1-butylpiperidinium bis(trifluoromethylsulfonyl)imide /
25 oxalic acid, 1-ethyl-3-methylpyridinium ethylsulfate /
oxalic acid, 1-butyl-4-methylpyridinium
bis(trifluoromethylsulfonyl)imide / oxalic acid, 1-
butylpyridinium tetrafluoroborate / oxalic acid,
trimethylbutylammonium
30 bis(trifluoromethylsulfonyl)imide / maleic acid,
tributylmethylammonium dicyanamide / maleic acid,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / maleic acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / maleic
35 acid, 2-hydroxyethyltrimethylammonium acetate /
maleic acid, 2-hydroxyethyltrimethylammonium lactate /

- maleic acid, 2-hydroxyethyltrimethylammonium
salicylate / maleic acid, tetrabutylammonium chloride /
maleic acid, 1,3-dimethylimidazolium methylsulfate /
maleic acid, 1,2,3-trimethylimidazolium methylsulfate /
5 maleic acid, 1-ethyl-3-methylimidazolium acetate /
maleic acid, 1-ethyl-3-methylimidazolium dicyanamide /
maleic acid, 1-ethyl-3-methylimidazolium methylsulfate
/ maleic acid, 1-ethyl-3-methylimidazolium thiocyanate /
maleic acid, 1-propyl-3-methylimidazolium acetate /
10 maleic acid, 1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / maleic acid, 1-butyl-
3-methylimidazolium acetate / maleic acid, 1-butyl-3-
methylimidazolium dicyanamide / maleic acid, 1-butyl-3-
methylimidazolium thiocyanate / maleic acid, 1-butyl-3-
15 methylimidazolium bromide / maleic acid, 1-butyl-3-
methylimidazolium hexafluorophosphate / maleic acid,
1-butyl-3-methylimidazolium tetrafluoroborate / maleic
acid, 1-octyl-3-methylimidazolium acetate / maleic acid,
1-octyl-3-methylimidazolium bromide / maleic acid, 1-
20 octyl-3-methylimidazolium tetrafluoroborate / maleic
acid, 1-methyl-1-butylpyrrolidinium dicyanamide /
maleic acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / maleic acid, 1-
methyl-1-butylpiperidinium
25 bis(trifluoromethylsulfonyl)imide / maleic acid, 1-ethyl-
3-methylpyridinium ethylsulfate / maleic acid, 1-butyl-4-
methylpyridinium bis(trifluoromethylsulfonyl)imide /
maleic acid, 1-butylpyridinium tetrafluoroborate / maleic
acid, trimethylbutylammonium
30 bis(trifluoromethylsulfonyl)imide / fumaric acid,
tributylmethylammonium dicyanamide / fumaric acid,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / fumaric acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / fumaric
35 acid, 2-hydroxyethyltrimethylammonium acetate /
fumaric acid, 2-hydroxyethyltrimethylammonium lactate

- / fumaric acid, 2-hydroxyethyltrimethylammonium
salicylate / fumaric acid, tetrabutylammonium chloride /
fumaric acid, 1,3-dimethylimidazolium methylsulfate /
fumaric acid, 1,2,3-trimethylimidazolium methylsulfate /
5 fumaric acid, 1-ethyl-3-methylimidazolium acetate /
fumaric acid, 1-ethyl-3-methylimidazolium dicyanamide /
fumaric acid, 1-ethyl-3-methylimidazolium methylsulfate
/ fumaric acid, 1-ethyl-3-methylimidazolium thiocyanate
/ fumaric acid, 1-propyl-3-methylimidazolium acetate /
10 fumaric acid, 1-propyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-butyl-
3-methylimidazolium acetate / fumaric acid, 1-butyl-3-
methylimidazolium dicyanamide / fumaric acid, 1-butyl-
3-methylimidazolium thiocyanate / fumaric acid, 1-butyl-
15 3-methylimidazolium bromide / fumaric acid, 1-butyl-3-
methylimidazolium hexafluorophosphate / fumaric acid,
1-butyl-3-methylimidazolium tetrafluoroborate / fumaric
acid, 1-octyl-3-methylimidazolium acetate / fumaric
acid, 1-octyl-3-methylimidazolium bromide / fumaric
20 acid, 1-octyl-3-methylimidazolium tetrafluoroborate /
fumaric acid, 1-methyl-1-butylpyrrolidinium dicyanamide
/ fumaric acid, 1-methyl-1-octylpyrrolidinium
bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-
methyl-1-butylpiperidinium
25 bis(trifluoromethylsulfonyl)imide / fumaric acid, 1-ethyl-
3-methylpyridinium ethylsulfate / fumaric acid, 1-butyl-
4-methylpyridinium bis(trifluoromethylsulfonyl)imide /
fumaric acid, 1-butylpyridinium tetrafluoroborate /
fumaric acid, trimethylbutylammonium
30 bis(trifluoromethylsulfonyl)imide / phthalic acid,
tributylmethylammonium dicyanamide / phthalic acid,
tributylmethylammonium
bis(trifluoromethylsulfonyl)imide / phthalic acid, tris(2-
hydroxyethyl)methylammonium methylsulfate / phthalic
35 acid, 2-hydroxyethyltrimethylammonium acetate /
phthalic acid, 2-hydroxyethyltrimethylammonium lactate

/ phthalic acid, 2-hydroxyethyltrimethylammonium
 salicylate / phthalic acid, tetrabutylammonium chloride /
 phthalic acid, 1,3-dimethylimidazolium methylsulfate /
 phthalic acid, 1,2,3-trimethylimidazolium methylsulfate /
 5 phthalic acid, 1-ethyl-3-methylimidazolium acetate /
 phthalic acid, 1-ethyl-3- methylimidazolium dicyanamide
 / phthalic acid, 1-ethyl-3-methylimidazolium
 methylsulfate / phthalic acid, 1-ethyl-3-
 methylimidazolium thiocyanate / phthalic acid, 1-propyl-
 10 3-methylimidazolium acetate / phthalic acid, 1-propyl-3-
 methylimidazolium bis(trifluoromethylsulfonyl)imide /
 phthalic acid, 1-butyl-3-methylimidazolium acetate /
 phthalic acid, 1-butyl-3-methylimidazolium dicyanamide
 / phthalic acid, 1-butyl-3-methylimidazolium thiocyanate
 15 / phthalic acid, 1-butyl-3-methylimidazolium bromide /
 phthalic acid, 1-butyl-3-methyl imidazolium
 hexafluorophosphate / phthalic acid, 1-butyl-3-
 methylimidazolium tetrafluoroborate / phthalic acid, 1-
 octyl-3-methylimidazolium acetate / phthalic acid, 1-
 20 octyl-3-methylimidazolium bromide / phthalic acid, 1-
 octyl-3-methylimidazolium tetrafluoroborate / phthalic
 acid, 1-methyl-1-butylpyrrolidinium dicyanamide /
 phthalic acid, 1-methyl-1-octylpyrrolidinium
 bis(trifluoromethylsulfonyl)imide / phthalic acid, 1-
 25 methyl-1-butylpiperidinium
 bis(trifluoromethylsulfonyl)imide / phthalic acid, 1-ethyl-
 3-methylpyridinium ethylsulfate / phthalic acid, 1-butyl-
 4-methylpyridinium bis(trifluoromethylsulfonyl)imide /
 phthalic acid, and 1-butylpyridinium tetrafluoroborate /
 30 phthalic acid.

[0052] In a further more preferable embodiment,
 exemplified embodiments of the combination of the ionic
 liquid and the acid (ionic liquid / acid) include 1-ethyl-3-
 methylimidazolium acetate / maleic acid, 1-propyl-3-
 35 methylimidazolium acetate / maleic acid, 1-butyl-3-
 methylimidazolium acetate / maleic acid, and 1-octyl-3-

methylimidazolium acetate / maleic acid.

[0053] The compounding ratio of the ionic liquid to the acid (ionic liquid / acid) is preferably 0.10 to 1.0, and more preferably 0.20 to 1.0, at an equivalence ratio.

5 This is because when the equivalence ratio is less than 0.10, the density of the cured film tends to decrease, and when it exceeds 1.0, the storage stability tends to decrease.

[0054] The acid can be used alone or in combination of two or more of any of these. The content of the acid is preferably 0.00020 to 10.0 mass %, more preferably 0.020 to 10.0 mass %, further preferably 0.020 to 8.0 mass %, based on the total mass of the composition according to the present invention.

15 [0055] (IV) Solvent

The solvent is not particularly limited as long as it uniformly dissolves or disperses the above-mentioned components (I) to (III) and additives added as needed. Examples of the solvent that can be used in the present invention 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, 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 and xylene; ketones such as methyl ethyl ketone, acetone, methyl amyl ketone, methyl

isobutyl ketone and cyclohexanone; alcohols such as ethanol, propanol, butanol, hexanol, cyclohexanol, ethylene glycol, glycerin, 3-methoxybutanol and 1,3-butanediol; esters such as ethyl lactate, butyl acetate, 3-methoxybutyl acetate, ethyl 3-ethoxy-propionate and methyl 3-methoxypropionate; and cyclic esters such as γ -butyrolactone, and preferably PGME, 3-methoxybutanol, 1,3-butanediol, PGMEA, ethyl lactate, butyl acetate, 3-methoxybutyl acetate. The solvent may be used alone or in combination of two or more of any of these.

[0056] So as to make workability improved by the adopted coating method, and in consideration of the permeability of the solution into the fine trenches and the film thickness required outside the trenches, the content of the solvent in the composition according to the present invention can be appropriately selected depending on the mass average molecular weight of the polysiloxane, distribution and structure thereof. The content of the solvent is preferably 50 to 98 mass %, more preferably 60 to 98 mass %, based on the total mass of the composition according to the present invention.

[0057] Although the composition according to the present invention essentially includes the above-mentioned (I) to (IV), further compounds can be optionally combined. The materials that can be combined are as described below. The content of the components other than (I) to (IV) in the entire composition is preferably 10 mass % or less, and more preferably 5 mass % or less, based on the total mass of the composition.

[0058] The composition according to the present invention can optionally comprise other additives. Examples of such additives include a surfactant, an adhesion enhancer, an antifoaming agent, a heat curing accelerator and the like.

[0059] The surfactant is added for the purpose of improving coating properties, developability, and the like. Examples of the surfactant that can be used in the present invention include nonionic surfactants, anionic surfactants, amphoteric surfactants, and the like.

5 [0060] Examples of the nonionic surfactant include, polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene oleyl ether and polyoxyethylene cetyl ether; polyoxyethylene fatty acid diester; polyoxyethylene fatty acid monoester;

10 polyoxyethylene polyoxypropylene block polymer; acetylene alcohol; acetylene alcohol derivatives such as polyethoxylate of acetylene alcohol; acetylene glycol; acetylene glycol derivatives such as polyethoxylate of

15 acetylene glycol; fluorine-containing surfactants, such as Fluorad (trade name, 3M Japan Limited), Megaface (trade name, DIC Corporation), Surflon (trade name, AGC Inc.); or organosiloxane surfactants such as KP341 (trade name, Shin-Etsu Chemical Co., Ltd.). Examples

20 of the above-mentioned acetylene glycol derivatives include 3-methyl-1-butyne-3-ol, 3-methyl-1-pentyne-3-ol, 3,6-dimethyl-4-octyne-3,6-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,5-dimethyl-1-hexyne-3-ol, 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-dimethyl-2,5-

25 hexanediol.

[0061] Examples of the anionic surfactant include ammonium salt or organic amine salt of alkyl diphenyl ether disulfonic acid, ammonium salt or organic amine salt of alkyl diphenyl ether sulfonic acid, ammonium salt or organic amine salt of alkyl benzene sulfonic acid, ammonium salt or organic amine salt of polyoxyethylene alkyl ether sulfuric acid, ammonium salt or organic amine salt of alkyl sulfuric acid.

30

[0062] Examples of the amphoteric surfactant include 2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolium betaine and lauric acid amide propyl hydroxysulfone

35

betaine.

[0063] These surfactants can be used alone or in combination of two or more of any of these, and the compounding amount thereof is usually 50 to 10,000 ppm, preferably 100 to 8,000 ppm, based on the composition according to the present invention.

[0064] The adhesion enhancer has an effect of preventing a pattern from being peeled off due to stress applied after baking when a cured film is formed using the composition according to the present invention. As the adhesion enhancer, imidazoles, silane coupling agents, and the like are preferred. Among imidazoles, 2-hydroxybenzimidazole, 2-hydroxyethylbenzimidazole, benzimidazole, 2-hydroxyimidazole, imidazole, 2-mercaptoimidazole and 2-aminoimidazole are preferable, and 2-hydroxybenzimidazole, benzimidazole, 2-hydroxyimidazole and imidazole are particularly preferably used.

[0065] As the antifoaming agent, alcohols (C₁₋₁₈), higher fatty acids such as oleic acid and stearic acid, higher fatty acid esters such as glycerin monolaurate, polyethers such as polyethylene glycols (PEG) (Mn: 200 to 10,000) and polypropylene glycols (PPG) (Mn: 200 to 10,000), silicone compounds such as dimethyl silicone oil, alkyl-modified silicone oil and fluorosilicone oil, and the above-mentioned organosiloxane-based surfactants are included. These can be used alone or in combination of a plurality of these, and the content thereof is preferably 0.1 to 3 mass% based on the total mass of the polysiloxane.

[0066] Examples of the heat curing accelerator include a thermal base generator, a thermal acid generator and the like. In the present invention, in the heat curing accelerator, the ionic liquid shall not be contained. Normally, by making a heat curing accelerator contained, the curing rate of the coating film during heating can be

increased. However, in the present invention, the ionic liquid fulfills the function of accelerating the curing of polysiloxane, so that curing can be exhibited even if any heat curing accelerator is not contained. Therefore, the content of the heat curing accelerator is preferably 0.01 mass % or less, more preferably 0.001 mass %. It is also a preferred aspect of the present invention that any heat curing accelerator is not contained.

[0067] Further, the composition according to the present invention can also be used as a composition having photosensitivity by further making a photobase generator, a photoacid generator and the like contained.

[0068] Method for manufacturing a cured film

The method for manufacturing a cured film according to the present invention comprises applying the composition according to the present invention above a substrate to form a coating film, and heating the coating film. In the present invention, "above a substrate" shall include a case where the composition is directly applied on the substrate and a case where the composition is applied on the substrate via one or more intermediate layers. The method for forming a cured film is described in process order as follows.

[0069] (1) Coating process

The shape of the substrate is not particularly limited and can be freely selected depending on the purpose. However, the composition according to the present invention is characterized in that it easily penetrates into narrow trenches and the like and can form a uniform cured film even inside the trenches, and therefore can be applied on a substrate with trenches and holes having a high aspect ratio. In particular, it can be applied on a substrate with at least one trench having a width of the deepest portion of 0.2 μm or less and an aspect ratio of 2 or more, and the like. Here, the shape of the trench is not particularly limited, and

the cross section may be any shape such as a rectangular shape, a forward tapered shape, a reverse tapered shape, and a curved surface shape. Further, both ends of the trench may be open or closed.

5 [0070] As a typical example of a substrate with at least one trench having a high aspect ratio, a substrate for an electronic device comprising a transistor element, a bit line, a capacitor, and the like is referred. In the production of such electronic devices, there is a case
10 that a process of forming an insulating film between a transistor element and a bit line called PMD, between a transistor element and a capacitor, between a bit line and a capacitor or between a capacitor and a metal wiring or an insulating film called IMD between a
15 plurality of metal wirings, or a process of filling isolation trenches is sometimes followed by a through-hole plating process of forming holes penetrating upward and downward through the material for filling a fine trench.

[0071] Application can be conducted by any method. It
20 can be freely selected from dip coating, roll coating, bar coating, brush coating, spray coating, doctor coating, flow coating, spin coating, slit coating, and the like. As the substrate on which the composition is applied, a suitable substrate such as a silicon substrate, a glass
25 substrate, a resin film, and the like can be used. Various semiconductor devices and the like can be formed on these substrates as needed. When the substrate is a film, gravure coating can also be utilized. If desired, a drying process can be additionally provided
30 after applying the film. Further, if necessary, the applying process can be repeated once, twice, or more to make the film thickness of the coating film to be formed as desired one.

[0072] (2) Pre-baking process
35 After forming the coating film by applying the composition, the coating film can be prebaked

(preheating treatment) in order to dry the coating film and reduce the residual amount of the solvent in the coating film.

[0073] (3) Curing process

5 A cured film is formed by heating the coating film. Here, in the present invention, the cured film means a film having an S2/S1 ratio of less than 0.003.

A hot plate or oven can be used as the heating apparatus used in the curing process. The heating
10 temperature in this curing process is not particularly limited as long as it is the temperature at which the cured film is formed, and it can be freely set. However, if silanol remains, the chemical resistance of the cured film may be insufficient or the dielectric constant of the
15 cured film may be increased. From this point of view, a relatively high heating temperature is generally selected, but when the composition according to the present invention is used, it can be cured at a relatively low temperature. In particular, it is preferable to heat at
20 500°C or lower, and more preferably 300°C or lower. On the other hand, in order to promote the curing reaction, the heating temperature is preferably 120°C or higher, more preferably 140°C or higher, and further preferably 170°C or higher. Further, the heating time is
25 not particularly limited, and when a hot plate is used, it is preferably 1 to 60 minutes, more preferably 1 to 30 minutes. The curing process is preferably performed in an air atmosphere.

[0074] Generation of voids may occur in this curing
30 process. In particular, when the number of organic groups contained in the polysiloxane decreases, the generation of voids tends to increase. However, when the composition of the present invention is used, the generation of voids can be suppressed even when the
35 number of organic groups contained in the polysiloxane is small.

[0075] The cured film formed using the composition according to the present invention can achieve good transparency, chemical resistance, environmental resistance, electrical insulation, heat resistance and the like. Therefore, it can be suitably used in various fields as an interlayer insulating film for low-temperature polysilicon, a buffer coat film for IC chips, a transparent protective film, and the like.

[0076] The method for manufacturing an electronic device comprises the method for manufacturing a cured film according to the above-mentioned present invention.

[0077] The present invention is explained more particularly below with reference to Examples and Comparative Examples, but the present invention is not limited by these Examples and Comparative Examples at all.

[0078] Gel permeation chromatography (GPC) is measured using Alliance (trademark) e2695 type high-speed GPC system (Japan Waters K.K.) and Super Multipore HZ-N type GPC column (Tosoh Corporation). The measurement is conducted using monodispersed polystyrene as a standard sample and cyclohexene as a developing solvent, under the measuring conditions of a flow rate of 0.6 ml/min and a column temperature of 40°C, and then mass average molecular weight (hereinafter sometimes referred to as Mw) is calculated as a relative molecular weight to the standard sample.

[0079] Synthesis Example 1: Polysiloxane A

In a 2L flask equipped with a stirrer, a thermometer and a condenser, 29.1 g of methyltrimethoxysilane, 0.6 g of phenyltrimethoxysilane, 0.4 g of tetramethoxysilane and 308 ml of PGME are charged and the mixture is cooled to 0.2°C. Then, 96.6 g of a 37 mass % tetra-n-butylammonium hydroxide methanol solution is added dropwise to the flask from a dropping funnel, the

5 mixture is stirred for 2 hours. Thereafter, 500 ml of n-propyl acetate is added, and then the mixture is cooled again to 0.2°C. 3% hydrochloric acid aqueous solution of 1.1 equivalence to TBAH is added, and then the mixture is stirred for 1 hour to neutralize. To the neutralized solution, 1,000 ml of n-propyl acetate and 250 ml of water are added, the reaction solution is separated into two layers, and the obtained organic layer is washed 3 times each with 250 cc of water and then concentrated under reduced pressure to remove water and the solvent. Then, PGMEA is added and adjusted to obtain a polysiloxane A solution.

10 The obtained polysiloxane A has a Mw of 2,630 and a S2/S1 of 0.041. In addition, the S2/S1 here is measured using the polysiloxane A solution in the same manner as the method for measuring a S2/S1 described later, except that heating is not performed.

[0080] Synthesis Example 2: Polysiloxane B

20 In a 2L flask equipped with a stirrer, a thermometer and a condenser, 32.5 g of a 40 mass % tetra-n-butylammonium hydroxide (TBAH) aqueous solution and 308 ml of 1-methoxy-2-propanol (PGME) are charged. Then, in a dropping funnel, a mixed solution of 19.6 g of methyltrimethoxysilane and 9.4 g of tetramethoxysilane is prepared. The mixed solution is added dropwise into the flask, and the mixture is stirred at room temperature for 2 hours. Thereafter, 500 ml of n-propyl acetate (n-PA) is added, then a 3% maleic acid aqueous solution of 1.1 equivalence to TBAH is added and the mixture is stirred for 1 hour to neutralize. To the neutralized solution, 500 ml of n-propyl acetate (n-PA) and 250 ml of water are added, the reaction solution is separated into two layers, and the obtained organic layer is washed 3 times each with 250 cc of water and then concentrated under reduced pressure to remove water and the solvent. Then, PGME is added and

adjusted to obtain a polysiloxane B solution.

The obtained polysiloxane B has a Mw of 2,180 and a S2/S1 of 0.10.

[0081] Synthesis Example 3: Polysiloxane C

5 In a 2L flask equipped with a stirrer, a thermometer and a condenser, 13.6 g of methyltrimethoxysilane, 63.2 g of tetramethoxysilane and 177 ml of acetone are charged and the mixture is cooled to 0.2°C. Then, 76.1 g of a 5.7 mol/L
10 hydrochloric acid aqueous solution is added dropwise from a dropping funnel into the flask, and the mixture is stirred in a room temperature water bath for 1 hour. After adding 200 ml of PGMEA, water and the solvent are removed by concentration under reduced pressure, and
15 3-methoxybutanol is added and adjusted to obtain a polysiloxane C solution.

The obtained polysiloxane C has a Mw of 730 and a S2/S1 of 0.14.

[0082] Synthesis Example 4: Polysiloxane D

20 In a 2L flask equipped with a stirrer, a thermometer and a condenser, 63.1 g of methyltrimethoxysilane, 92.7 g of tetramethoxysilane and 250 ml of acetone are charged and the mixture is cooled to 0.2°C. Then, 76.1 g of a 5.7 mol/L
25 hydrochloric acid aqueous solution is added dropwise from a dropping funnel into the flask, and the mixture is stirred in a room temperature water bath for 1 hour. After adding 200 ml of PGMEA, water and the solvent are removed by concentration under reduced pressure, and
30 1,3-butanediol is added and adjusted to obtain a polysiloxane D solution.

The obtained polysiloxane D has a Mw of 7,720 and a S2/S1 of 0.12.

[0083] Preparation of polysiloxane compositions

35 With the compositions and contents shown in Tables 1 to 7 below, polysiloxane compositions of

Examples 101 to 105, 201 to 206, 301 to 305, 401 to 405, 501 and 502, and Comparative Examples 101 to 103, 201 to 203 and 501 are prepared. In the tables, the numerical values of the compositions mean mass %.

5 [Table 1]

Table 1

			Example				
			101	102	103	104	105
Composition	(I)Polysiloxane A		7.06	7.02	7.04	7.00	6.98
	(II)Ion liquid A		0.070	0.070	0.070	-	-
	(II)Ion liquid B		-	-	-	0.56	-
	(II)Ion liquid C		-	-	-	-	0.014
	Thermal base generator A		-	-	-	-	-
	(III)Maleic acid		0.048	0.072	0.11	-	-
	(III)Citraconic acid		-	-	-	-	0.11
	(III)Oxalic acid		-	-	-	0.25	-
	(III)Phthalic acid		-	-	-	-	-
	(IV)PGMEA		balance	balance	balance	balance	balance
	Total		100	100	100	100	100
Evaluation	Film thickness uniformity	200°C 2min	0.47%	0.51%	0.52%	0.52%	0.49%
	Film loss	200°C 2min	5.46%	5.22%	5.64%	5.48%	5.88%
	S2/S1	200°C 2min	0.0020	0.0013	0.0017	0.0015	0.00093
	Filling property	250°C 2min	A	A	A	A	A

[Table 2]

Table 2

Table 2			Comparative Example		
			101	102	103
Composition	(I)Polysiloxane A		7.01	7.00	7.04
	(II)Ion liquid A		-	-	-
	(II)Ion liquid B		-	-	-
	(II)Ion liquid C		-	-	-
	Thermal base generator A		-	-	0.11
	(III)Maleic acid		-	0.11	-
	(III)Citraconic acid		-	-	-
	(III)Oxalic acid		-	-	-
	(III)Phthalic acid		-	-	-
	(IV)PGMEA		balance	balance	balance
	Total		100	100	100
Evaluation	Film thickness uniformity	200℃2min	6.18%	6.88%	0.46%
	Film loss	200℃2min	17.1%	14.3%	5.53%
	S2/S1	200℃2min	0.0226	0.0194	0.0035
			C	C	B
	Filling property	250℃2min	A	A	B

[Table 3]

Table 3

Table 3			Example					
			201	202	203	204	205	206
Composition	(I)Polysiloxane B		7.00	6.99	6.98	7.00	7.01	7.00
	(II)Ion liquid A		0.091	0.091	0.091	-	-	0.00035
	(II)Ion liquid B		-	-	-	0.014	-	-
	(II)Ion liquid C		-	-	-	-	0.63	-
	Thermal base generator A		-	-	-	-	-	-
	(III)Maleic acid		0.062	0.093	0.14	-	-	0.00054
	(III)Citraconic acid		-	-	-	0.02	-	-
	(III)Oxalic acid		-	-	-	-	-	-
	(III)Phthalic acid		-	-	-	-	0.64	-
	(IV)PGME		balance	balance	balance	balance	balance	balance
	Total			100	100	100	100	100
Evaluation	Film thickness uniformity	200°C 2min	1.06%	0.89%	0.87%	0.92%	0.95%	0.94%
	Film loss	200°C 2min	9.76%	6.85%	9.32%	9.11%	8.56%	9.88%
	S2/S1	200°C 2min	0.00119	0.00103	0.00100	0.00111	0.00153	0.00210
			A	A	A	A	A	A
	Filling property	250°C 2min	A	A	A	A	A	A

[Table 4]

Table 4

			Comparative Example		
			201	202	203
Composition	(I)Polysiloxane B		7.00	7.00	6.99
	(II)Ion liquid A		-	-	-
	(II)Ion liquid B		-	-	-
	(II)Ion liquid C		-	-	-
	Thermal base generator A		-	-	0.099
	(III)Maleic acid		-	0.14	-
	(III)Citraconic acid		-	-	-
	(III)Oxalic acid		-	-	-
	(III)Phthalic acid		-	-	-
	(IV)PGME		balance	balance	balance
	Total		100	100	100
Evaluation	Film thickness uniformity	200°C2min	1.19%	1.52%	1.14%
	Film loss	200°C2min	14.5%	10.9%	12.1%
	S2/S1	200°C2min	0.00702	0.0102	0.00350
			C	C	B
Evaluation	Filling property	250°C2min	A	A	B

[Table 5]

Table 5

			Example				
			301	302	303	304	305
Composition	(I)Polysiloxane C		7.03	7.00	7.01	6.99	7.00
	(II)Ion liquid B		0.14	0.14	-	-	0.18
	(II)Ion liquid C		-	-	0.35	-	-
	(II)Ion liquid D		-	-	-	0.59	-
	Thermal base generator A		-	-	-	-	-
	(III)Maleic acid		-	-	-	0.56	-
	(III)Citraconic acid		0.13	-	-	-	0.27
	(III)Oxalic acid		-	0.14	-	-	-
	(III)Phthalic acid		-	-	0.36	-	-
	(IV)3-methoxybutanol		balance	balance	balance	balance	balance
	Total		100	100	100	100	100
Evaluation	Film thickness uniformity	200°C 2min	1.24%	1.19%	1.57%	1.54%	1.68%
	Film loss	200°C 2min	9.86%	9.88%	9.55%	9.52%	9.89%
	S2/S1	200°C 2min	0.00082	0.00088	0.00050	0.00052	0.00077
			A	A	A	A	A

[Table 6]

Table 6			Example				
			401	402	403	404	405
Composition	(I) Polysiloxane D		6.98	7.03	6.99	7.01	7.00
	(II) Ion liquid A		0.084	0.084	-	-	0.0035
	(II) Ion liquid B		-	-	-	0.0070	-
	(II) Ion liquid D		-	-	0.59	-	-
	Thermal base generator A		-	-	-	-	-
	(III) Maleic acid		0.23	0.086	-	-	-
	(III) Citraconic acid		-	-	-	-	0.0027
	(III) Oxalic acid		-	-	-	0.0150	-
	(III) Phthalic acid		-	-	0.47	-	-
	(IV) 1,3-butanediol		balance	balance	balance	balance	balance
	Total		100	100	100	100	100
Evaluation	Film thickness uniformity	200 °C 2min	0.68%	0.71%	0.73%	0.65%	0.77%
	Film loss	200 °C	5.21%	5.85%	5.33%	5.55%	6.12%
	S2/S1	200 °C	0.00077 A	0.00075 A	0.00050 A	0.00190 A	0.00290 A

[Table 7]

Table 7			Example		Comparative Example
			501	502	501
Composition	(I) Polysiloxane B		7.00	7.00	7.00
	(II) Ion liquid A		0.70	0.70	-
	Thermal base generator A		-	-	-
	(III) Citraconic acid		0.81	-	-
	(III) Acetylenedicarboxylic acid		-	0.70	-
	(IV) PGME		balance	balance	balance
	Total		100	100	100
Evaluation	Film thickness uniformity	150 °C 2min	0.96%	0.93%	1.21%
	Film loss	150 °C 2min	5.11%	5.08%	11.4%
	S2/S1	150 °C 2min	0.0022 A	0.0013 A	0.056 C

In the tables,

- 5 ionic liquid A: 1-ethyl-3-methylimidazolium acetate (EMIMAc),
 ionic liquid B: 1-butyl-3-methylimidazolium dicyanamide,
 ionic liquid C: 2-hydroxyethyltrimethylammonium

acetate,
ionic liquid D: 1-methyl-1-butylpyrrolidinium
dicyanamide, and
thermal base generator A: manufactured by San-Apro
Ltd.

[0084] Evaluation of film thickness uniformity

The polysiloxane composition is applied on a 4-inch Si wafer at 1,000 rpm using a spin coater (1HDX2, manufactured by Mikasa Co., Ltd.). The coated wafer is cured in the air at 200°C or at 150°C, for 2 minutes. The cured film thickness is measured at 19 points on the diameter using a spectroscopic ellipsometer (M-2000V, manufactured by J.A. Woollam Co., Ltd.), and 3 times of the coefficient of variation is taken as the film thickness uniformity. The results are shown in Tables 1 to 7.

[0085] Evaluation of film loss

The polysiloxane composition is applied on a 4-inch Si wafer at 1,000 rpm using a spin coater (1HDX2, manufactured by Mikasa Co., Ltd.). The coated film thickness is measured at 19 points on the diameter using a spectroscopic ellipsometer (M-2000V, manufactured by J.A. Woollam) and the average value thereof is used. The coated wafer is cured in the air at 200°C or at 150°C, for 2 minutes. The cured film thickness is measured in the same manner as the coated film thickness. The results are shown in Tables 1 to 7.

Film loss (%) = (coated film thickness - cured film thickness) / coated film thickness x 100

[0086] S2/S1

The polysiloxane composition is dropped on a 4-inch Si wafer, spin-coated at 1,000 rpm, and then cured on a hot plate at 200°C or at 150°C, for 2 minutes. Measurement of the FT-IR spectrum is performed at room temperature using FTIR-6100 (JASCO Corporation). In consideration of noise, a baseline correction is conducted, and the integrated intensity of

an absorption band (S2) assigned to Si-OH having a peak in the range of $900 \pm 100 \text{ cm}^{-1}$ and the integrated intensity of an absorption band (S1) assigned to Si-O having a peak in the range of $1,100 \pm 100 \text{ cm}^{-1}$ are measured, thereby calculating a value of S2/S1.

Incidentally, there is a possibility that the foot of the absorption band assigned to Si-OH and the foot of the absorption band assigned to Si-O are overlapped; however, in such a case, the wavenumber corresponding to the minimal point between the two absorption bands in the spectrum is set as their boundary. The same applies to the case where the foot of the other absorption band overlaps with the foot of the absorption band assigned to Si-OH or Si-O.

The obtained S2/S1 values are evaluated according to the following criteria. The results are shown in Tables 1 to 7.

A: less than 0.003

B: 0.003 or more and less than 0.006

C: 0.006 or more

[0087] Evaluation of filling properties

The polysiloxane composition is applied on a Si wafer having a trench (width: 20 nm, height: 500 nm) by spin coating, and after the application, it is heated on a hot plate at 250°C for 2 minutes. After that, the cross-sectional shape is observed with a scanning electron microscope (S-4700, manufactured by Hitachi High-Technologies Corporation) to confirm the presence or absence of voids. The evaluation criteria are as follows, and the obtained results are shown in Tables 1 to 4.

A: the trenches are filled and no voids are confirmed.

B: the trenches are filled and voids are confirmed.

[0088] Evaluation of storage stability

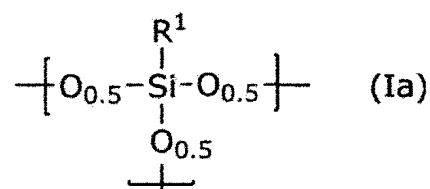
When a polysiloxane composition consisting of 7 mass % of the polysiloxane B, 0.7 mass % of the ionic

5 liquid A, 0.7 mass % of maleic acid and the balance of PGME, and a polysiloxane composition consisting of 7 mass % of the polysiloxane B, 0.7 mass % of the ionic liquid A and the balance of PGME are stored at room temperature for 2 days and the appearance of these are observed, the composition containing maleic acid shows no change in appearance, but in the composition containing no maleic acid, gelation is observed.

Patent Claims

1. A polysiloxane composition comprising:
 - (I) a polysiloxane,
 - (II) an ionic liquid,
 - (III) an acid, and
 - (IV) a solvent.

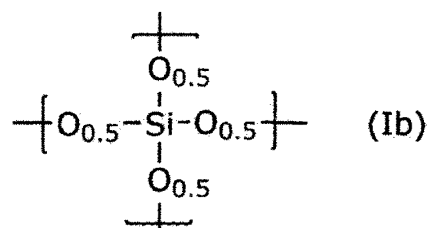
2. The composition according to claim 1, wherein the polysiloxane (I) comprises a repeating unit represented by the following formula (Ia) and a repeating unit represented by the following formula (Ib), and has silanol at the end or side chain, and when the polysiloxane is measured and analyzed by the FT-IR method, S2/S1 that is a ratio of the integrated intensity S1 of an absorption band assigned to Si-O in the range of $1100 \pm 100 \text{ cm}^{-1}$ to the integrated intensity S2 of an absorption band assigned to SiOH in the range of $900 \pm 100 \text{ cm}^{-1}$ is 0.020 to 0.20:



where

R¹ is hydrogen, a mono- to trivalent, linear, branched or cyclic, saturated or unsaturated, C₁₋₃₀ aliphatic hydrocarbon group, or a mono- to trivalent, C₆₋₃₀ aromatic hydrocarbon group, the aliphatic hydrocarbon group and the aromatic hydrocarbon group are each unsubstituted or substituted with fluorine, hydroxy or C₁₋₈ alkoxy, in the aliphatic hydrocarbon group and the aromatic hydrocarbon group, methylene is not replaced, or one or more methylene are replaced with oxy, imide or carbonyl, provided that R¹ is neither hydroxy nor alkoxy,

when R¹ is divalent or trivalent, R¹ connects each Si contained in a plurality of repeating units;



3. The composition according to claim 2, wherein R¹ is hydrogen, a linear, branched or cyclic, C₁₋₆ alkyl, or C₆₋₁₀ aryl.
4. The composition according to any one of claims 1 to 3, wherein the cation of the ionic liquid is at least one cation selected from the group consisting of an imidazolium type ion, a pyrrolidinium type ion, a piperidinium type ion, a pyridinium type ion, and an ammonium type ion.
5. The composition according to any one of claims 1 to 4, wherein the anion of the ionic liquid is at least one anion selected from the group consisting of a formate ion, an acetate ion, a propionate ion, a lactate ion, an oleate ion, a salicylate ion, a dicyanamide ion, a cyanamide ion, a thiocyanate ion, a methyl sulfate ion, an ethyl sulfate ion, a hydrogen sulfate ion, a methane sulfonate ion, a trifluoromethane sulfonate ion, a p-toluene sulfonate ion, a bis(trifluoromethylsulfonyl)imide ion, a bis(fluorosulfonyl)imide ion, a methyl carbonate ion, a hydrogen carbonate ion, a diethyl phosphate ion, a dibutyl phosphate ion, a hexafluorophosphate ion, a tetrafluoroborate ion, a chlorine ion, and a bromine ion.
6. The composition according to any one of claims 1 to 5, wherein the mass average molecular weight of the polysiloxane is 500 to 10,000 as measured by the gel permeation chromatography.

7. The composition according to any one of claims 1 to 6, wherein the compounding ratio of the ionic liquid to the polysiloxane (ionic liquid / polysiloxane) is 0.000030 to 0.10 by mass ratio.
8. The composition according to any one of claims 1 to 6, wherein the compounding ratio of the ionic liquid to the acid (ionic liquid / acid) is 0.10 to 1.0 at an equivalence ratio.
9. The composition according to any one of claims 1 to 8, wherein the acid is an organic acid.
10. The composition according to any one of claims 1 to 9, wherein the ratio of the number of the repeating units represented by the formula (Ib) is 8% or more based on the total number of the repeating units contained in the polysiloxane.
11. The composition according to any one of claims 1 to 10, wherein the solvent (IV) is at least one selected from the group consisting of propylene glycol monomethyl ether, 3-methoxybutanol, 1,3-butanediol, propylene glycol monomethyl ether acetate, ethyl lactate, butyl acetate and 3-methoxybutyl acetate.
12. The composition according to any one of claims 1 to 11, wherein the content of the solvent (IV) is 50 to 98 mass % based on the total mass of the composition.
13. A method for manufacturing a cured film, comprising applying the composition according to any one of claims 1 to 12 above a substrate to form a coating film, and heating the coating film.
14. The method for manufacturing a cured film according to

claim 12, wherein the heating is performed at a temperature of 120°C or higher.

15. A method for manufacturing an electronic device, comprising the method for manufacturing a cured film according to claim 13 or 14.