more kinds of members, the composite body being equipped with the composite member and the polymer.

Further, another aspect of the invention is to provide a composition containing a polymer, in which the composition can achieve both the ease of remaining the polymer on a specific member and the difficulty of remaining the polymer on other member, when applied to two or more kinds of composite members.

Solution to Problem

[0005] Specific means for addressing the above problems are as follows.

<1> A method for manufacturing a composite body, the method containing:

a composition preparation process of preparing a composition that contains a polymer having a cationic functional group and having a weight average molecular weight of from 2,000 to 1,000,000, and that has a pH of from 2.0 to 11.0;

a composite member preparation process of preparing a composite member that includes a member A and a member B, a surface of the member B having an isoelectric point that is lower than an isoelectric point of a surface of the member A by 2.0 or more and the isoelectric point of the member B being from 1.0 to 7.5, and that satisfies a relationship: the isoelectric point of a surface of the member B < the pH of the composition < the isoelectric point of a surface of the member A; and

an application process of applying the composition to the surface of the member A and the surface of the member B included in the composite member.

<2> The method for manufacturing a composite body according to <1>, wherein the member A contains at least one element selected from the group consisting of Cu, Al, Ti, ~~Ni,~~ Fe, Sn, Cr, Mn, Ni, Pt, Zn and Mg, and the member B contains silica.

<3> The method for manufacturing a composite body according to <1> or <2>, wherein the member A contains Cu, and the member B contains silica.

<4> The method for manufacturing a composite body according to any one of <1> to <3>, wherein a content of sodium and a content of potassium in the composition are each 10 ppb by ~~weight~~ mass or less, on an elemental basis.

<5> The method for manufacturing a composite body according to any one of <1> to <4>, the method further comprising a heating process of heating the composite member to which the composition has been applied, under a condition of a temperature of from 70°C to 125°C.

<6> The method for manufacturing a composite body according to any one of <1> to <5>, wherein the member B contains a porous material.

<7> The method for manufacturing a composite body according to any one of <1> to

<6>, wherein the polymer has a cationic functional group equivalent weight of from 27 to 430.

<8> The method for manufacturing a composite body according to any one of <1> to <7>, wherein the polymer is a polyethyleneimine or a derivative of a polyethyleneimine.

<9> The method for manufacturing a composite body according to any one of <1> to <8>, wherein the polymer has a branching degree of 48% or more.

<10> The method for manufacturing a composite body according to any one of <1> to <9>, wherein the composition further contains a monocarboxylic acid compound.

<11> The method for manufacturing a composite body according to <10>, wherein the monocarboxylic acid compound does not have a hydroxyl group or an amino group, and has a van der Waals volume of 40 cm^3/mol or more.

<12> The method for manufacturing a composite body according to any one of <1> to <11>, wherein the composite member satisfies a relationship: the isoelectric point of a surface of the member B < the pH of the composition < {(the isoelectric point of a surface of the member A) - 1.0}.

<13> The method for manufacturing a composite body according to any one of <1> to <12>, the method further comprising a cleaning process of cleaning the composite member to which the composition has been applied, with a rinsing liquid at a temperature of from 15°C to 100°C.

<14> The method for manufacturing a composite body according to <13>, wherein the rinsing liquid comprises an acid having, in one molecule, at least one of a moiety that blocks active species or a functional group that forms a bond with the polymer when heated.

<15> The method for manufacturing a composite body according to any one of <1> to <14>, the method further comprising a high temperature heating process of heating the composite member to which the composition has been applied, under a condition of a temperature of from 200°C to 425°C.

<16> The method for manufacturing a composite body according to any one of <1> to <15>, wherein the composite member comprises a substrate and, on the substrate, a conductive part as the member A and an insulating layer as the member B.

[0006] <17> A composition that comprises a polymer having a cationic functional group and having a weight average molecular weight of from 2,000 to 1,000,000 and a branching degree of 48% or more, and that has a pH of from 2.0 to 11.0, wherein a content of sodium and a content of potassium in the composition are each 10 ppb by ~~weight~~ mass or less, on an elemental basis.

<18> The composition according to <17>, further comprising a monocarboxylic acid

In the invention, the "isoelectric point" refers to a pH value of the solvent in which the zeta potential of a substrate surface in water, which is measured in accordance with an electromigration method, a streaming potential method, an electroosmosis method, or the like, becomes zero. Further, as examples of the isoelectric point of the surface of a solid, isoelectric points described in G. A. Parks, Chemical Reviews, vol. 65, pages 177 to 198 (1965) can be described.

[0017] As described above, the composite member satisfies the relationship: the isoelectric point of a surface of the member B < the pH of the composition < the isoelectric point of a surface of the member A.

From the viewpoint of more effectively exhibiting the effects of the invention, it is preferable that the composite member satisfies the relationship: the isoelectric point of a surface of the member B < the pH of the composition < {(the isoelectric point of a surface of the member A) - 1.0}.

In the above relationship, particularly, when the relationship: the pH of the composition < {(the isoelectric point of a surface of the member A) - 1.0} is satisfied, the polymer more hardly adheres to the member A, and thus, the polymer more hardly remains on the member A.

[0018] The composite member may have only one of member A, or may have plural thereof.

It is preferable that the member A contains at least one element (hereinafter, also referred to as a "specific metal element") selected from the group consisting of Cu, Al, Ti, ~~Ni,~~ Fe, Sn, Cr, Mn, Ni, Pt, Zn, and Mg.

In this case, the member A may contain a metal element other than the specific metal element or a non-metal element (for example, nitrogen (N), oxygen (O), or the like).

It is preferable that the member A contains the specific metal element as the main component.

Here, the "main component" indicates the component that is included at the highest content percentage (% by mass) (hereinafter the same applies).

The content percentage of the specific metal element in the member A is preferably 50% by mass or higher, preferably 80% by mass or higher, and preferably 90% by mass or higher.

[0019] The member A is not limited to have a form of a member capable of being present independently, and may have, for example, a form of a member provided on a substrate.

In a case in which the member A is a member provided on a substrate, this member A can be formed in accordance with a known means such as sputtering, vapor deposition, CVD (Chemical Vapor Deposition), metal plating, or ALD (Atomic Layer Deposition). In this

that a polymer layer is hardly formed on the exposed face 20a in the process of applying the composition to the exposed face 20a.

Accordingly, for example, it is possible to omit the process of removing the polymer layer on the exposed face 20a. For example, even in a case in which the process of removing the polymer layer is omitted, a state, in which the polymer layer is formed on the exposed faces of the respective insulating layers, but the exposed face 20a is not covered with the polymer layer, can be provided.

[0087] For the numerical value of the van der Waals volume of the specific monocarboxylic acid compound, the value described in "CHEMICAL PROPERTIES HANDBOOK" (edited by YAWS, published by McGraw Hill) is used.

It is more preferable that the van der Waals volume of the specific monocarboxylic acid compound is from 40 cm^3/mol to 85 cm^3/mol.

[0088] As the specific monocarboxylic acid compound (the monocarboxylic acid compound that does not have either a hydroxyl group or an amino group, and has a van der Waals volume of 40 cm^3/mol or more), specifically, propionic acid, ~~picolinic acid,~~ butyric acid, valeric acid, hexanoic acid, heptanoic acid, acrylic acid, picolinic acid, and the like are preferable. Particularly, propionic acid and picolinic acid are preferable.

[0089] Moreover, in a case in which the surface of the member A, to which the composition is to be applied, is subjected to the pretreatment described above (pretreatment using, for example, benzotriazole, phenanthroline, bipyridyl, or the like), before the application of the composition to the surface of the member A, even when the specific monocarboxylic acid compound is not used but formic acid or acetic acid is used, it is possible to make the polymer hardly adhere to the surface of the member A in the application process of applying the composition to the surface of the member A.

[0090] The composition in the invention may further contain a hydrophobilizing agent.

As the hydrophobilizing agent, those commonly used may be used, and a chelating agent that forms a hydrophobic group on the surface of the member A, such as 8-quinolinol, benzotriazole, phenanthroline, bipyridyl, 2,2'-bipyridine, 1,10-phenanthroline, tribipyridine, acetylacetone, triaminopropane, tribipyridine, or phthalic acid, and the like are preferable.

[0091] It is preferable that a content of sodium and a content of potassium in the composition in the invention are each 10 ppb by ~~weight~~ mass or less, on an elemental basis. Herewith, deterioration in electric properties (for example, in a case in which the composite body includes a transistor, operation failure of transistor or the like), in the case of using an electronic device as the composite body, can be suppressed.

[0092] A particularly preferable form of the composition in the invention is a form of a

composition that contains a polymer having a cationic functional group and having a weight average molecular weight of from 2,000 to 1,000,000 and a branching degree of 48% or more, and that has a pH of from 2.0 to 11.0, in which a content of sodium and a content of potassium in the composition are each 10 ppb by ~~weight~~ mass or less, on an elemental basis.

In this form, it is more preferable that the composition further contains a monocarboxylic acid compound.

In this form, a preferable range of the pH is as described above.

Further, in the case of using the composition in the invention as a semiconductor sealing composition, this form is particularly preferable.

[0093] Moreover, the composition in the invention is preferable not only for a semiconductor sealing composition, but also for a sealing composition in various electronic devices (a print wiring substrate, a display device, and the like).

[0094] The composition in the invention can contain a solvent, in addition to the polymer, if necessary.

The solvent is not particularly limited as far as the solvent is a solvent that uniformly dissolves the polymer and hardly forms a micelle. Examples of such a solvent may include water (preferably, ultrapure water) and water-soluble organic solvents (for example, alcohols and the like). In the invention, from the viewpoint of micelle forming property, it is preferable to use water or a mixture of water and a water-soluble organic solvent, as the solvent. Further, the boiling point of the solvent is not particularly limited, but is preferably 210°C or lower and more preferably 160°C or lower. When the boiling point of the solvent is within the above range, the solvent can be easily removed at a low temperature.

With regard to the components of the composition, the components of a composition described, for example, in WO 2010/137711 and WO 2012/033172, can be referred to, as appropriate.

[0095] The composition in the invention preferably has an average particle diameter measured by a dynamic light scattering method of 150 nm or less.

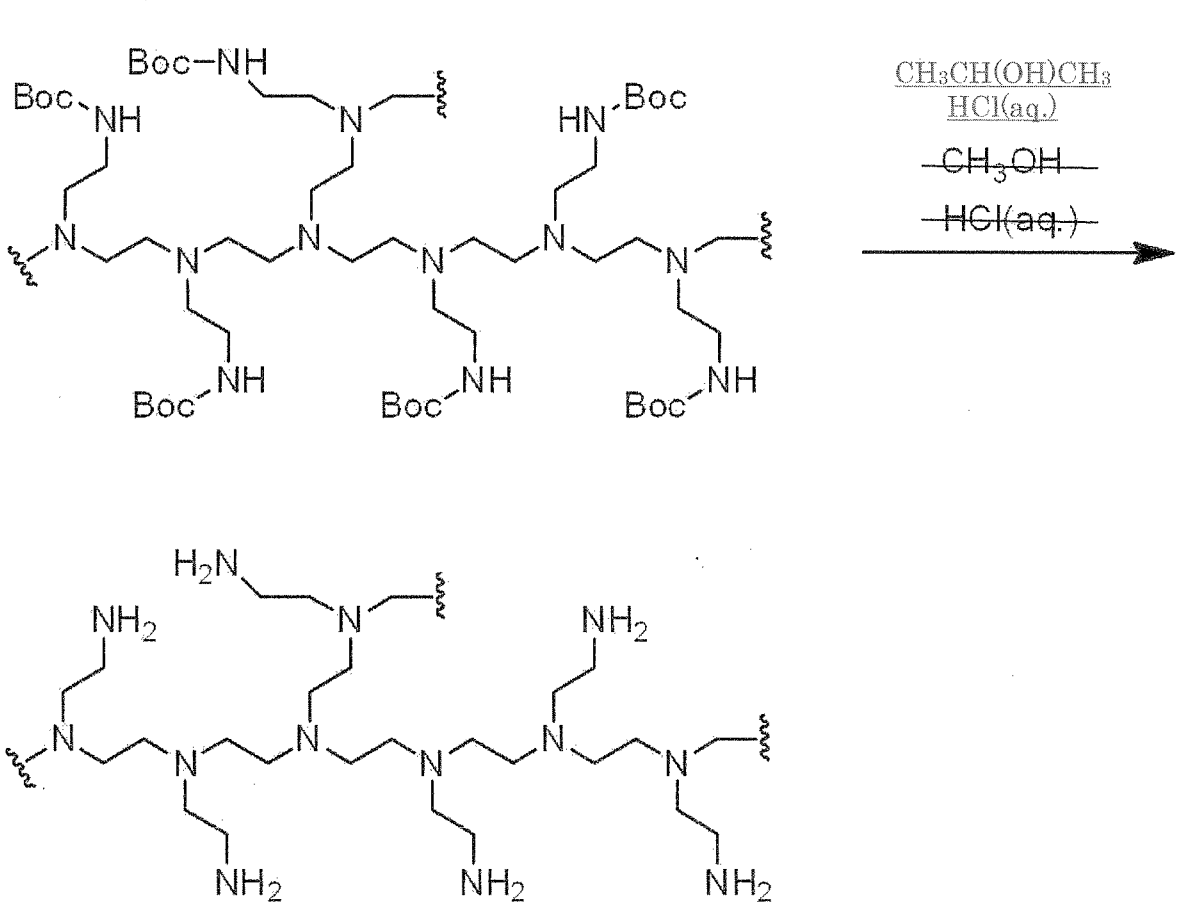
When the average particle diameter is 150 nm or less, the covering property of the polymer layer with respect to the member B is further enhanced. For example, even in a case in which a concave portion, an opening, or the like is formed in the member B, the wall faces of the concave portion, the opening, or the like can be suitably covered with the polymer layer.

Here, the average particle diameter is measured by a dynamic light scattering method using an ELSZ-2, manufactured by Otsuka Electronics Co., Ltd., and is obtained as a cumulant average particle diameter. Regarding the measurement conditions, measurement is

[0138] (Synthesis of Highly Branched Polyethyleneimine 1)

Highly branched polyethyleneimine 1 was synthesized according to the following Reaction Scheme 2, using the modified polyethyleneimine 1 as the starting material.

[0139] - Reaction Scheme 2 -



[0140] The detailed operation of Reaction Scheme 2 above is as follows.

124 mL of 12N hydrochloric acid were slowly added to the isopropanol solution of modified polyethyleneimine 1. The solution thus obtained was stirred under heating at 50°C for 4 hours, while being careful about generation of gas. Together with the generation of gas, a gum-like reaction product was generated in the reaction system. After the completion of the generation of gas, the reaction system was cooled. After cooling, the solvent that had been separated from this gum-like reaction product was removed, and then the resulting reaction product was washed three times with 184 mL of methanol. The reaction product that had been washed was dissolved in water, and chlorine ions were removed by using an anion exchange polymer, to obtain an aqueous solution containing 58 g of highly branched polyethyleneimine 1.

- NMR Measurement Results of Highly Branched Polyethyleneimine 1 -

^{1}H-NMR (D_2O); δ 2.8-2.4 (br. m)

TABLE 7

	Added Acid	pH of Composition (at 25°C)	Thickness of Polymer Layer on Si (nm)	Thickness of Polymer Layer on Cu (nm)
Example 3D	Formic acid	5.0	8.5	0.2
Comparative Example 2D	none	10.5	6.6	9.8

[0175] As shown in Table 7, in Example 3D, the thickness of the polymer layer on copper (Cu) was 0.2 nm. Accordingly, by subjecting the copper (Cu) surface to the BTA treatment, the amount of the polymer adhered was smaller by about 2 nm in thickness, as compared with Example 3A (Table 1) that was not subjected to the BET treatment.

In Comparative Example 2D, the thickness of the polymer layer on copper (Cu) was 9.8 nm, and the polymer remained thick.

[0176] [Examples 9E and 10E]

In Examples 9EB and 10EB, samples that had not been subjected to cleaning treatment were prepared. Namely, after forming the polymer layer on a silicon wafer and on a copper substrate, respectively, samples that had been subjected to the soft bake were prepared. With regard to these samples, measurement of the thickness of the polymer layer and measurement of the thickness of the polymer layer on copper were carried out, similar to Example 1A.

The measurement results are shown in Table 8.

[0177]

TABLE 8

	Added Acid	pH of Composition (at 25°C)	Thickness of Polymer Layer on Si (nm)	Thickness of Polymer Layer on Cu (nm)
Example 9E	Propionic acid	4.5	3.8	-2.3
Example 10E	Propionic acid	5.5	8.3	-2.1

[0178] As shown in Table 8, in Examples 9E and 10E, a polymer layer was not observed on the copper (Cu). Since the copper oxide on the surface of the copper (Cu) that serves as the substrate was etched by acid, the thickness of the polymer layer on copper (Cu) was a minus numerical value.

[0179] The disclosures of Japanese Patent Application No. 2013-067452 filed on March 27, 2013 and Japanese Patent Application No. 2013-179751 filed on August 30, 2013 are

CLAIMS

1. A method for manufacturing a composite body, the method comprising:

a composition preparation process of preparing a composition that contains a polymer having a cationic functional group and having a weight average molecular weight of from 2,000 to 1,000,000, and that has a pH of from 2.0 to 11.0;

a composite member preparation process of preparing a composite member that includes a member A and a member B, a surface of the member B having an isoelectric point that is lower than an isoelectric point of a surface of the member A by 2.0 or more and the isoelectric point of the member B being from 1.0 to 7.5, and that satisfies a relationship: the isoelectric point of a surface of the member B < the pH of the composition < the isoelectric point of a surface of the member A; and

an application process of applying the composition to the surface of the member A and the surface of the member B included in the composite member.

2. The method for manufacturing a composite body according to claim 1, wherein the member A contains at least one element selected from the group consisting of Cu, Al, Ti, ~~Ni,~~ Fe, Sn, Cr, Mn, Ni, Pt, Zn and Mg, and the member B contains silica.

3. The method for manufacturing a composite body according to claim 1 or claim 2, wherein the member A contains Cu, and the member B contains silica.

4. The method for manufacturing a composite body according to claim 1 or claim 2, wherein a content of sodium and a content of potassium in the composition are each 10 ppb by ~~weight~~ mass or less, on an elemental basis.

5. The method for manufacturing a composite body according to claim 1 or claim 2, the method further comprising a heating process of heating the composite member to which the composition has been applied, under a condition of a temperature of from 70°C to 125°C.

6. The method for manufacturing a composite body according to claim 1 or claim 2, wherein the member B contains a porous material.

7. The method for manufacturing a composite body according to claim 1 or claim 2, wherein the polymer has a cationic functional group equivalent weight of from 27 to 430.

2, wherein the composite member comprises a substrate and, on the substrate, a conductive part as the member A and an insulating layer as the member B.

17. A composition that comprises a polymer having a cationic functional group and having a weight average molecular weight of from 2,000 to 1,000,000 and a branching degree of 48% or more, and that has a pH of from 2.0 to 11.0, wherein a content of sodium and a content of potassium in the composition are each 10 ppb by ~~weight~~ mass or less, on an elemental basis.

18. The composition according to claim 17, further comprising a monocarboxylic acid compound.

19. The composition according to claim 17 or claim 18, being a semiconductor sealing composition.