

DESCRIPTION

TITLE OF INVENTION: SILICON-CONTAINING RESIN COMPOSITION
PURIFIED PRODUCT MANUFACTURING METHOD, PATTERN FORMATION
METHOD, AND SILICON-CONTAINING RESIN COMPOSITION PURIFIED
5 PRODUCT

TECHNICAL FIELD

[0001]

The present invention relates to a silicon-containing resin composition purified
10 product manufacturing method, a pattern formation method, and a silicon-containing
resin composition purified product.

Priority is claimed on Japanese Patent Application No. 2023-042391, filed on
March 16, 2023, the content of which is incorporated herein by reference.

BACKGROUND ART

15 [0002]

In recent years, in the manufacturing of semiconductor elements and liquid
crystal display elements, advances in the lithography technology have led to a rapid
progress in the field of pattern fining. These pattern fining techniques typically involve
shortening the wavelength (increasing the energy) of the exposure light source.

20 Resist materials are required to have lithography characteristics such as
sensitivity to these exposure light sources and resolution that enables reproduction of a
pattern having fine dimensions. As a resist material that satisfies these requirements, a
chemical amplification-type resist composition containing a base material component
that exhibits changed solubility in a developing solution under action of acid and an acid
25 generator component that generates an acid upon exposure has been used in the related

art.

[0003]

As the pattern fining progresses, the influence of impurities present in the resist material is likely to be apparent in the pattern formation. In a case where a pattern
 5 having a dimension of several tens of nanometers is formed, defects due to scum after development, adhesion of foreign substances to a pattern surface, and the like are a serious problem.

On the other hand, in the manufacturing of a resist composition, purification is generally carried out by passing the composition through a filter in order to remove
 10 impurities in the composition. For example, Patent Document 1 proposes a manufacturing method for a photoresist composition, including both a step of passing a photoresist composition through a filter made of nylon and a step of passing the photoresist composition through a filter made of a polyolefin resin or a fluororesin.

Citation List

15 Patent Document

[0004]

Patent Document 1: Japanese Unexamined Patent Application, First Publication
 No. 2004-212975

SUMMARY OF INVENTION

20 Technical Problem

[0005]

In addition, in the formation of a pattern having fine dimensions, a resin film that is mainly formed of a base material component of a resist material is formed to be a thin film. In addition, as such a resist material, a material having etching resistance is
 25 required in order to fulfill the function as a mask for substrate processing. On the other

hand, a silicon-containing resin is generally used as a base material component.

However, in a case where a silicon-containing resin composition in which a silicon-containing resin is used as a base material component is purified through a step of carrying out filtration through a filter in the related art, there is such a defect that defects in pattern transfer are likely to occur due to the presence of defects (coating defects) in the coating film, which results in a problem of reduced yield.

[0006]

The present invention has been made in consideration of the above circumstances, and an object of the present invention is to provide a silicon-containing resin composition purified product manufacturing method in which impurities are further reduced and the occurrence of defects during the formation of a coating film is suppressed and a silicon-containing resin composition purified product manufactured by the above-described manufacturing method, as well as a pattern formation method using the silicon-containing resin composition purified product.

15 Solution to Problem

[0007]

In order to solve the above problem, the present invention has employed the following configuration.

[0008]

20 A first aspect of the present invention is a silicon-containing resin composition purified product manufacturing method including a step of filtering a silicon-containing resin composition with a filter having a porous structure in which adjacent spherical cells are connected to each other, in which the filter has a porous membrane containing at least one kind of resin selected from the group consisting of polyimide and polyamide-imide, and the silicon-containing resin composition contains a silicon-containing resin (A)

25

having a main chain consisting of a siloxane bond, a siloxane bond-containing cage compound (C) other than the silicon-containing resin (A), and an organic solvent component (S).

[0009]

5 A second aspect of the present invention is a pattern formation method including a step of obtaining a silicon-containing resin composition purified product by the silicon-containing resin composition purified product manufacturing method according to the first aspect; and a step of forming a silicon-containing resist lower layer film on a support using the silicon-containing resin composition purified product, forming an upper layer resist film on the silicon-containing resist lower layer film using an upper layer resist film composition, forming an upper layer resist pattern on the upper layer resist film, transferring a pattern to the silicon-containing resist lower layer film by etching using the upper layer resist pattern as a mask, and transferring a pattern to the support by etching using, as a mask, the silicon-containing resist lower layer film having the transferred pattern.

[0010]

 A third aspect of the present invention is a silicon-containing resin composition purified product containing a silicon-containing resin (A) having a main chain consisting of a siloxane bond, a siloxane bond-containing cage compound (C) other than the silicon-containing resin (A), and an organic solvent component (S), in which the number of counting target objects having a size of 0.135 μm or more is less than 0.2 objects/mL, where the counting target objects are counted by a light scattering-type liquid-borne particle counter.

[0011]

25 A fourth aspect of the present invention is a pattern formation method including

forming a silicon-containing resist lower layer film on a support using the silicon-containing resin composition purified product according to the third aspect; forming an upper layer resist film on the silicon-containing resist lower layer film using an upper layer resist film composition; forming an upper layer resist pattern on the upper layer resist film and transferring a pattern to the silicon-containing resist lower layer film by etching using the upper layer resist pattern as a mask; and transferring a pattern to the support by etching using, as a mask, the silicon-containing resist lower layer film having the transferred pattern.

Advantageous Effects of Invention

10 [0012]

According to the present invention, it is possible to provide a silicon-containing resin composition purified product manufacturing method in which impurities are further reduced and the occurrence of defects during the formation of a coating film is suppressed and a silicon-containing resin composition purified product manufactured by the above-described manufacturing method, as well as a pattern formation method using the silicon-containing resin composition purified product.

BRIEF DESCRIPTION OF DRAWINGS

[0013]

[FIG. 1] A view schematically showing one embodiment of an interconnection pore constituting a polyimide-based resin porous membrane.

DESCRIPTION OF EMBODIMENTS

[0014]

In the present specification and the scope of the present claims, the term "aliphatic" is a relative concept used with respect to "aromatic" and defines a group, a compound, or the like that has no aromaticity.

The “alkyl group” includes linear, branched, and cyclic monovalent saturated hydrocarbon groups, unless otherwise specified. The same applies to the alkyl group of an alkoxy group.

5 The “alkylene group” includes linear, branched, and cyclic divalent saturated hydrocarbon groups, unless otherwise specified.

The “halogenated alkyl group” is a group obtained by substituting part or all of hydrogen atoms of an alkyl group with a halogen atom. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

10 The “fluorinated alkyl group” or a “fluorinated alkylene group” is a group obtained by substituting part or all of hydrogen atoms of an alkyl group or an alkylene group with a fluorine atom.

The term “constitutional unit” indicates a monomer unit that constitutes the formation of a polymeric compound (a resin, a polymer, or a copolymer).

15 The description of “may have a substituent” means that a case where a hydrogen atom (-H) is substituted with a monovalent group or a case where a methylene group (-CH₂-) is substituted with a divalent group.

The “exposure” is used as a general concept that includes irradiation with any form of radiation.

[0015]

20 The term "polyimide-based resin" means one or both of polyimide and polyamide-imide. The polyimide and the polyamide-imide may each have at least one functional group selected from the group consisting of a carboxy group, a salt-type carboxy group, and an -NH- bond.

25 A porous membrane containing at least one of polyimide and polyamide-imide may be referred to as a "polyimide-based resin porous membrane". A porous

membrane containing polyimide may be referred to as a "polyimide porous membrane".

A porous membrane containing polyamide-imide may be referred to as a "porous polyamide-imide membrane".

[0016]

5 In the present specification and the scope of the present claims, asymmetric carbon may be present depending on a structure represented by a chemical formula, and enantiomers or diastereomers may be present. In that case, these isomers are represented by one chemical formula. These isomers may be used alone or in the form of a mixture.

10 [0017]

(Silicon-containing resin composition purified product manufacturing method)

A silicon-containing resin composition purified product manufacturing method according to a first aspect of the present invention includes a step of filtering a silicon-containing resin composition with a filter having a porous structure in which adjacent
15 spherical cells are connected to each other (hereinafter, this step will also be referred to as a "step (i)").

The filter has a porous membrane containing at least one kind of resin selected from the group consisting of polyimide and polyamide-imide.

The silicon-containing resin composition contains a silicon-containing resin (A)
20 having a main chain consisting of a siloxane bond, a siloxane bond-containing cage compound (C) other than the silicon-containing resin (A), and an organic solvent component (S).

[0018]

By the step (i), the impurities are reduced by adsorbing defect sources (a minute
25 gel component, an inorganic ultrafine particle component capable of interacting with a

minute gel component, and an inorganic ion component, and the like) during the formation of a coating film, from the silicon-containing resin composition to the filter. In this manner, a silicon-containing resin composition purified product, which can suppress the occurrence of defects during the formation of a coating film, is obtained.

5 According to such a manufacturing method, in particular, by using a filter having a porous membrane that has a porous structure in which adjacent spherical cells are connected to each other and contains at least one kind of resin selected from the group consisting of polyimide and polyamide-imide, highly polar components and polymers, which have been difficult to be removed in the related art, are sufficiently
10 removed from the silicon-containing resin composition, and among them, the highly polar polymer is specifically removed.

In addition, in the step (i), a metal component as an impurity is also sufficiently removed from the silicon-containing resin composition. This metal component may be originally contained in the component constituting the silicon-containing resin
15 composition; however, it may also be mixed from a silicon-containing resin composition transfer path such as a pipe or a joint of a manufacturing device. In the step (i), it is possible to effectively remove, for example, iron, nickel, zinc, chromium, and the like, which are easily mixed from a manufacturing device or the like.

[0019]

20 <Step (i)>

The step (i) is a step of filtering the silicon-containing resin composition with a filter having a porous structure in which adjacent spherical cells are connected to each other.

[0020]

25 <<Filter>>

The filter that is used in the present step has a porous structure in which adjacent spherical cells are connected to each other. For example, such a filter may be made of a simple body of a porous membrane in which adjacent spherical cells are connected to each other, or it may be a filter in which another filtering medium is used together with the porous membrane.

Examples of other filtering medium include a nylon membrane, a polytetrafluoroethylene membrane, a tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer (PFA) membrane, and a membrane obtained by modifying these membranes. [0021]

In such a filter, regions of the porous membrane before and after a liquid is allowed to pass are preferably sealed so that a supply liquid and a filtrate of the silicon-containing resin composition are separated without being mixed. Examples of the method for this sealing include a method of processing the porous membrane by adhesion with light (UV) curing, adhesion with heat (including adhesion by an anchoring effect (heat welding or the like)), adhesion using an adhesive, or the like, and a method of carrying out processing by adhering the porous membrane and another filtering medium by an assembling method or the like. Examples of such a filter include those in which such a porous membrane described above is provided in an outer container made of a thermoplastic resin (polyethylene, polypropylene, PFA, polyether sulfone (PES), polyimide, polyamide-imide, or the like).

In such a filter, examples of the form of the porous membrane include a planar shape and a pipe shape in which opposite sides of the porous membrane are merged.

The surface of the pipe-shaped porous membrane is preferably pleated from the viewpoint of increasing the area that comes into contact with the supply liquid.

[0022]

· In regard to "porous membrane in which adjacent spherical cells are connected to each other"

The "porous membrane in which adjacent spherical cells are connected to each other" provided in such a filter has an interconnection pore in which adjacent spherical
5 cells are connected to each other.

The interconnection pore is formed from individual pores (cells) that impart porosity to the porous membrane. Such a pore includes a pore in which almost the entire inner surface of the pore is a curved surface, and it may include a pore having a shape other than this shape.

10 [0023]

In the present specification, a pore in which almost the entire inner surface of the pore is a curved surface is referred to as a "spherical cell" or a "substantially spherical pore". In the spherical cell (the substantially spherical pore), the inner surface of the pore forms a substantially spherical space. The spherical cell is easily formed in a case
15 where fine particles that are used in the manufacturing method for a polyimide-based resin porous membrane described later are substantially spherical.

The phrase "substantially spherical" is a concept including a true sphere. However, it is not necessarily limited to the true sphere and is a concept including a substantially spherical one. The phrase "substantially spherical" means that a sphericity
20 defined by a ratio of a major axis to a minor axis, which is represented by a value obtained by dividing the major axis by the minor axis of the particle, is within 1 ± 0.3 . Here, in the spherical cell, such a sphericity is preferably within 1 ± 0.1 and more preferably within 1 ± 0.05 .

In the porous membrane in which adjacent spherical cells are connected to each
25 other, the adjacent spherical cells form at least a part of the interconnection pore.

[0024]

FIG. 1 is a view schematically showing one embodiment of an interconnection pore constituting a porous membrane.

In each of a spherical cell 1a and a spherical cell 1b in the porous membrane
5 according to the present embodiment, almost the entire inner surface is a curved surface, and a substantially spherical space is formed.

The spherical cell 1a and the spherical cell 1b are adjacent to each other, and an interconnection pore 5 in which an overlapping portion Q of the spherical cell 1a and the spherical cell 1b adjacent to each other penetrates between the cells is formed. A
10 filtration target flows through the interconnection pore 5, for example, in the direction (the arrow direction) from the spherical cell 1a toward the spherical cell 1b.

[0025]

As described above, in the porous membrane having a structure in which adjacent spherical cells are connected to each other, it is preferable that a plurality of
15 pores (spherical cells or interconnection pores) are connected to form a flow path of a filtration target as a whole.

The "flow path" is generally formed by the individual "pores" and/or "interconnection pores" that are connected to each other. The individual pores are formed, for example, by removing individual fine particles present in a polyimide-based
20 resin-fine particle composite membrane in a subsequent step in the manufacturing method for a polyimide-based resin porous membrane described later. In addition, the interconnection pore is pores adjacent to each other, which are formed in a portion where individual fine particles have been in contact with each other, where the portion is present in the polyimide-based resin-fine particle composite membrane, by removing the
25 fine particles in a subsequent step in the manufacturing method for a polyimide-based

resin porous membrane described later.

In the porous membrane, a spherical cell and an interconnection pore in which adjacent spherical cells are connected to each other are formed, and thus the degree of porosity is increased. In addition, in the porous membrane, a spherical cell or an
5 interconnection pore opens on a surface of the porous membrane,, and an interconnection pore that opens on one surface is connected to the inside of the porous membrane and opens on the other (on the back side) surface, and thus a flow path in which a fluid can pass through the inside of the porous membrane is formed. As a result, according to the porous membrane, in a case where a filtration target flows through the flow path, foreign
10 substances contained in a filtration target are removed from the filtration target before filtration.

[0026]

Since the porous membrane has, in the inside, a flow path obtained by causing interconnection pores formed by spherical cells having a curved surface on the inner
15 surface thereof to be continuous, the surface area of the inner surface of the spherical cells is large. As a result, not only a filtration target can pass through the inside of the porous membrane but also the frequency of contacting with the inner surface of the spherical cell increases in a case where the filtration target passes while coming into contact with the curved surfaces of the individual spherical cells, and thus foreign
20 substances that are present in the filtration target are adsorbed by the inner surface of the spherical cell, and the foreign substances are easily removed from the filtration target.

[0027]

The porous membrane preferably has a structure in which spherical cells having an average spherical cell diameter of 10 to 2,500 nm are connected to each other. The
25 average spherical cell diameter of the spherical cells is more preferably 15 to 1,000 nm

and still more preferably 20 to 400 nm. Any combination of the upper limit value and the lower limit value may be allowed, and for example, the average spherical cell diameter of the spherical cells may be 20 to 2,500 nm.

[0028]

5 The flow path included in the inside of the "porous membrane in which adjacent spherical cells are connected to each other" may have, in addition to the above-described spherical cells and the interconnection pores between the spherical cells, pores having other shapes or interconnection pores including these pores.

 In addition, the spherical cell may further have a recessed part on the inner
10 surface thereof. For example, a pore having a pore diameter smaller than that of the spherical cell may be formed in the recessed part, where the pore opens on the inner surface of the spherical cell.

[0029]

 Examples of the "porous membrane in which adjacent spherical cells are
15 connected to each other" include those containing a resin, which may be substantially made of only a resin, and includes those in which the resin in the entire porous membrane is preferably 95% by mass or more, more preferably 98% by mass or more, and still more preferably 99% by mass or more.

[0030]

20 The porous membrane contains a polyimide-based resin. A porous membrane containing a polyimide-based resin is excellent in terms of the foreign substance removability or strength and the stability of lithography characteristics before and after filtration.

 The porous membrane contains at least one of polyimide and polyamide-imide
25 as a resin and preferably contains at least polyimide. The porous membrane may

contain only polyimide as a resin or may contain only polyamide-imide; however, it preferably contains only polyimide.

[0031]

It is particularly preferable that in the "porous membrane in which adjacent
5 spherical cells are connected to each other", 95% by mass or more of the entire porous membrane is at least one of polyimide and polyamide-imide.

Hereinafter, a porous membrane (a polyimide-based resin porous membrane) in which adjacent spherical cells are connected to each other, which contains a polyimide-based resin as the resin, will be described.

10 [0032]

· Polyimide-based resin porous membrane

The polyimide-based resin may have at least one functional group selected from the group consisting of a carboxy group, a salt-type carboxy group, and an -NH- bond.

The polyimide-based resin preferably has the above functional group in a moiety
15 other than the terminal of the main chain. Preferred examples having the above functional group in a moiety other than the terminal of the main chain include a polyamic acid.

[0033]

In the present specification, the term "salt-type carboxy group" means a group
20 obtained by substituting a hydrogen atom in a carboxy group with a cation component. The term "cation component" may be a cation itself in a state of being completely ionized, may be a cation constitutional element in a state of being ionically bonded to -COO⁻ and virtually uncharged, and may be a partially charged cation constitutional element having a partial charge in a state of being an intermediate state between the two
25 above.

In a case where the "cation component" is an M ion component consisting of an n-valent metal M, the cation itself is represented by M^{n+} , and the cation constitutional element is an element represented by " $M_{1/n}$ " in " $-COOM_{1/n}$ ".

[0034]

5 Examples of the "cation component" include a cation in a case where a compound mentioned as a compound contained in an etching liquid described later is ion-dissociated. Representative examples thereof include an ion component and an organic alkali ion component. For example, in a case where the alkali metal ion component is a sodium ion component, the cation itself is a sodium ion (Na^+), and the
10 cation constitutional element is an element represented by " Na " in " $-COONa$ ". The partially charged cation constitutional element is $Na^{\delta+}$.

The cation component is not particularly limited, and examples thereof include an inorganic component of NH_4^+ and an organic component such as $N(CH_3)_4^+$. Examples of the inorganic component include alkali metals such as Li, Na, and K; and
15 metal elements such as alkaline earth metals such as Mg and Ca. Examples of the organic component include an organic alkali ion component. Examples of the organic alkali ion component include quaternary ammonium cations represented by NH_4^+ , for example, NR_4^+ (all of four R's represent organic groups and may be the same or different from each other). The organic group as R is preferably an alkyl group and more
20 preferably an alkyl group having 1 to 6 carbon atoms. Examples of the quaternary ammonium cation include $N(CH_3)_4^+$.

[0035]

The state of the cation component in the salt-type carboxy group is not particularly limited, and generally depends on the environment in which the polyimide-
25 based resin is present, for example, an environment in an aqueous solution, an

environment in an organic solvent, and a dry environment. In a case where the cation component is a sodium ion component, for example, there is a possibility that -COO^- and Na^+ are dissociated in a case of being in an aqueous solution, and there is a high possibility that -COONa is not dissociated in a case of being in an organic solvent or in a dry environment.

[0036]

The polyimide-based resin may have at least one functional group selected from the group consisting of a carboxy group, a salt-type carboxy group, and an -NH- bond; however, in a case of having at least one of these, it generally has both a carboxy group and/or a salt-type carboxy group and an -NH- bond. The polyimide-based resin may have only a carboxy group, may have only a salt-type carboxy group, or may have both a carboxy group and a salt-type carboxy group, in a case where the carboxy group and/or the salt-type carboxy group is concerned. The ratio between the carboxy group and the salt-type carboxy group contained in the polyimide-based resin may vary, for example, depending on the environment in which the polyimide-based resin is present, even in a case where the polyimide-based resin is the same, and it is also affected by the concentration of the cation component.

[0037]

In the case of polyimide, the total of the numbers of moles of the carboxy group and the salt-type carboxy group contained in the polyimide-based resin is generally equimolar to that of the -NH- bond.

In particular, in the manufacturing method for a polyimide porous membrane described later, in a case where a carboxy group and/or a salt-type carboxy group is formed from a part of imide bonds in the polyimide, an -NH- bond is also formed substantially at the same time. The total of the numbers of moles of the carboxy group

to be formed and the salt-type carboxy group to be formed is equimolar to that of the -NH-bond formed.

In the case of the manufacturing method for a porous polyamide-imide membrane, the total of the numbers of moles of the carboxy group and the salt-type carboxy group in the polyamide-imide is not necessarily equimolar to that of the -NH-bond, and it depends on the conditions for chemical etching or the like in the etching (the decyclization of the imide bond) step described later.

[0038]

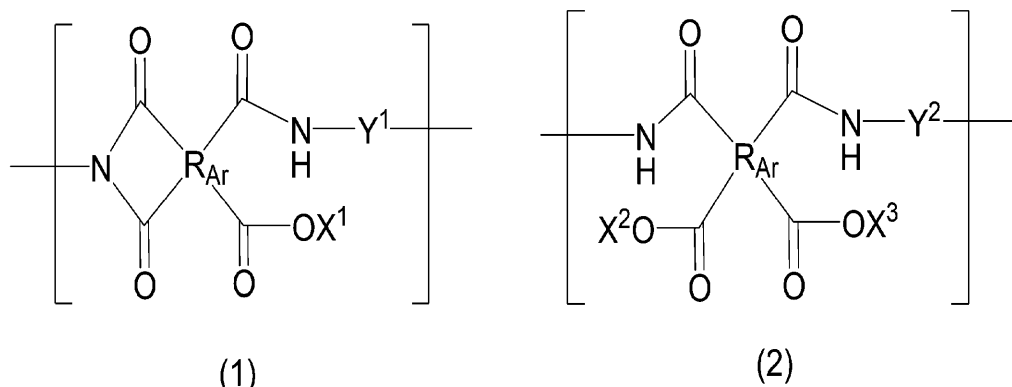
The polyimide-based resin preferably has, for example, at least one kind of constitutional unit selected from the group consisting of constitutional units each represented by General Formulae (1) to (4).

In the case of polyimide, it is preferable to contain at least one kind of constitutional unit selected from the group consisting of a constitutional unit represented by General Formula (1) and a constitutional unit represented by General Formula (2).

In the case of polyamide-imide, it is preferable to contain at least one kind of constitutional unit selected from the group consisting of a constitutional unit represented by General Formula (3) and a constitutional unit represented by General Formula (4).

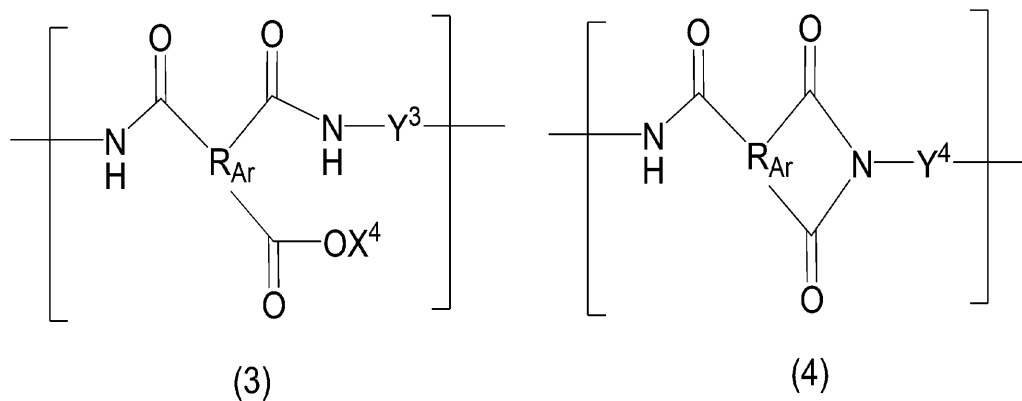
[0039]

[Chemical Formula 1]



[0040]

[Chemical Formula 2]



[0041]

5 In General Formulae (1) to (3) described above, X^1 to X^4 may be the same or different from each other and are a hydrogen atom or a cation component.

R_{Ar} represents an aryl group, and examples thereof include the same one as the aryl group represented by R_{Ar} , to which a carbonyl group is bonded, in each of a constitutional unit represented by General Formula (5) constituting a polyamic acid

10 described later or a constitutional unit represented by General Formula (6) constituting an aromatic polyimide.

Y^1 to Y^4 each independently represent a divalent residue excluding the amino group of the diamine compound, and examples thereof include the same one as the arylene group represented by R'_{Ar} , to which N is bonded, in each of a constitutional unit represented by General Formula (5) constituting a polyamic acid described later or a constitutional unit represented by General Formula (6) constituting an aromatic polyimide.

15

[0042]

The polyimide-based resin may be one obtained by decyclizing a part of imide bonds ($-N[-C(=O)]_2$) of a general polyimide or polyamide-imide, thereby having each of

20

the constitutional unit represented by General Formula (1) or General Formula (2) in the case of polyimide and the constitutional unit represented by General Formula (3) in the case of polyamide-imide.

[0043]

- 5 The polyimide-based resin porous membrane may contain a polyimide-based resin obtained by decyclizing part of imide bonds, thereby having at least one functional group selected from the group consisting of a carboxy group, a salt-type carboxy group, and an -NH- bond.

[0044]

- 10 The non-change rate in a case where a part of imide bonds are decyclized is determined by the following procedures (1) to (3).

- Procedure (1): For a polyimide-based resin porous membrane that does not undergo the etching (the decyclization of imide bond) step described later (however, in a case where a varnish for producing the porous membrane contains a polyamic acid, it is
15 assumed that the imidization reaction has been substantially completed in the step of sintering an unsintered composite membrane), an area of a peak that represents the imide bond, measured by a Fourier transform infrared spectroscopy (FT-IR) apparatus, is divided by an area of a peak that represents benzene, also measured by the Fourier transform infrared spectroscopy (FT-IR) apparatus, to determine a value represented by a
20 value (X01).

- Procedure (2): For a polyimide-based resin porous membrane obtained by using the same polymer (the varnish) as that of the porous membrane from which the above value (X01) has been determined, where the polyimide-based resin porous membrane has undergone the etching (the decyclization of imide bond) step described later, an area of a
25 peak that represents the imide bond, measured by a Fourier transform infrared

spectroscopy (FT-IR) apparatus, is divided by an area of a peak that represents benzene, also measured by the Fourier transform infrared spectroscopy (FT-IR) apparatus, to determine a value represented by a value (X02).

Procedure (3): the non-change rate is calculated according to the following
5 expression.

$$\text{Non-change rate (\%)} = (X02)/(X01) \times 100$$

[0045]

The non-change rate in the polyimide-based resin porous membrane is preferably in a range of 60% or more, more preferably in a range of 70% to 99.5%, and
10 still more preferably in a range of 80% to 99%.

In the case of a porous membrane containing polyamide-imide, the non-change rate may be 100% since an -NH- bond is contained.

[0046]

In the case of a polyimide porous membrane, an area of a peak that represents
15 the imide bond, measured by an FT-IR apparatus, is divided by an area of a peak that represents benzene, also measured by the FT-IR apparatus, to determine a value that is denoted by the "imidization rate".

The imidization rate regarding the value (X02) determined in the above procedure (2) is preferably 1.2 or more, more preferably in a range of 1.2 to 2, and still
20 more preferably in a range of 1.3 to 1.6, particularly preferably in a range of 1.30 to 1.55, and most preferably 1.35 or more and less than 1.5. In addition, the imidization rate regarding the value (X01) determined in the above procedure (1) is preferably 1.5 or more.

As the numerical value of such an imidization rate becomes relatively larger, it
25 means that the number of imide bonds becomes larger, that is, the number of decyclized

imide bonds described above becomes smaller.

[0047]

.. Manufacturing method for polyimide-based resin porous membrane

The polyimide-based resin porous membrane can be manufactured by a method
5 including a step (hereinafter, referred to as an "etching step") of forming a carboxy group
and/or a salt-type carboxy group from a part of imide bonds in polyimide and/or
polyamide-imide.

In the etching step, in a case where a carboxy group and/or a salt-type carboxy
group is formed from a part of imide bonds in the polyimide, an -NH- bond theoretically
10 equimolar to these groups is also formed substantially at the same time.

[0048]

In a case where the resin contained in the polyimide-based resin porous
membrane substantially consists of polyamide-imide, the porous membrane already has
an -NH- bond even without undergoing the etching step and exhibits good adsorption
15 power to foreign substances in the filtration target. In such a case, the etching step is
not always necessary since it is not needed to slow down the flow rate of the filtration
target; however, it is preferable to provide the etching step from the viewpoint of more
effectively achieving the object of the present invention.

[0049]

20 In the manufacturing method for a polyimide-based resin porous membrane, it is
preferable to carry out the etching step after preparing a molding membrane containing
polyimide and/or polyamide-imide as a main component (hereinafter, may be abbreviated
as a "polyimide-based resin molded membrane").

The polyimide-based resin molded membrane to be subjected to the etching step
25 may be porous or may be non-porous.

In addition, the form of the polyimide-based resin molded membrane is not particularly limited; however, it preferably has a thin shape of a membrane or the like, and it is more preferably porous and has a thin shape of a membrane or the like from the viewpoint that the degree of porosity in the polyimide-based resin porous membrane to
5 be obtained can be increased.

[0050]

As described above, the polyimide-based resin molded membrane may be non-porous in a case where the etching step is carried out. However, in that case, it is preferable to make the polyimide-based resin molded membrane porous after the etching
10 step.

The method for making the polyimide-based resin molded membrane porous before or after the etching step is preferably a method including a [Fine particle removal] step of removing fine particles from a composite membrane (hereinafter, referred to as a "polyimide-based resin-fine particle composite membrane") of polyimide and/or
15 polyamide-imide and fine particles, to make the composite membrane porous.

[0051]

Examples of the manufacturing method for a polyimide-based resin porous membrane include the following manufacturing method (a) and manufacturing method (b).

20 The manufacturing method (a): a method of etching a composite membrane of polyimide and/or polyamide-imide and fine particles before a [Fine particle removal] step.

The manufacturing method (b): a method of carrying out an etching step, after a [Fine particle removal] step, on a polyimide-based resin molded membrane made porous
25 by the [Fine particle removal] step.

Among these, the latter manufacturing method (b) is preferable from the viewpoint that the degree of porosity in the polyimide-based resin porous membrane to be obtained can be further increased.

[0052]

- 5 An example of the manufacturing method for a polyimide-based resin porous membrane will be described below.

[0053]

[Preparation of varnish]

- 10 A fine particle dispersion liquid in which fine particles are dispersed in an organic solvent in advance is mixed with polyamic acid, or polyimide or polyamide-imide at any ratio or tetracarboxylic acid dianhydride and a diamine are polymerized to be polyamic acid in the above fine particle dispersion liquid, or further, the above polyamic acid is imidized to be polyimide, whereby a varnish is prepared.

- 15 The viscosity of the varnish is preferably in a range of 300 to 2,000 cP (0.3 to 2 Pa·s) and more preferably in a range of 400 to 1,800 cP (0.4 to 1.8 Pa·s). In a case where the viscosity of the varnish is within the above range, a membrane can be formed more uniformly.

The viscosity of the varnish can be measured with an E-type rotational viscometer under a temperature condition of 25°C.

20 [0054]

- In the varnish, resin fine particles are mixed with polyamic acid, or polyimide or polyamide-imide so that the ratio of the fine particles/the polyimide-based resin is preferably in a range of 1 to 4 (mass ratio) and more preferably in a range of 1.1 to 3.5 (mass ratio) in a case of being sintered (dried in a case where sintering is optional) to form a polyimide-based resin-fine particle composite membrane.
- 25

In addition, fine particles are mixed with polyamic acid, or polyimide or polyamide-imide so that the volume ratio of the fine particles/the polyimide-based resin is preferably in a range of 1.1 to 5 and more preferably in a range of 1.1 to 4.5 in a case of being made to form a polyimide-based resin-fine particle composite membrane.

5 In a case where the mass ratio or the volume ratio is equal to or larger than the preferred lower limit value of the above range, pores having a suitable density as a porous membrane can be easily obtained, and in a case where it is equal to or smaller than the preferred upper limit value of the above range, problems such as the increase in viscosity and the cracking in the membrane hardly occur, and membrane formation can
10 be stably achieved.

In addition, in the present specification, the volume ratio indicates a value obtained at 25°C.

[0055]

... Fine particle

15 As the fine particle material, any material can be used without particular limitation as long as it is insoluble in an organic solvent that is used for the varnish and can be selectively removed after the membrane formation.

Examples of the fine particle material include metal oxides such as silica (silicon dioxide), titanium oxide, alumina (Al_2O_3), and calcium carbonate as the inorganic
20 material. Examples of organic materials include organic polymers such as a high molecular weight olefin (polypropylene, polyethylene, or the like), polystyrene, an acrylic resin (methyl methacrylate, isobutyl methacrylate, polymethyl methacrylate (PMMA), or the like), an epoxy resin, cellulose, polyvinyl alcohol, polyvinyl butyral, polyester, polyether, and polyethylene.

25 Among the above, the inorganic material is preferably silica such as colloidal

silica since micropores having a curved surface on the inner surface are easily formed in the porous membrane. The organic material is preferably an acrylic resin such as PMMA.

[0056]

5 The resin fine particles can be selected from, for example, typical linear polymers and publicly known depolymerizable polymers without particular limitation depending on the intended purpose. The typical linear polymer is a polymer in which the molecular chains of the polymer are randomly cleaved during thermal decomposition. The depolymerizable polymer is a polymer that decomposes into monomers during
10 thermal decomposition. Any polymer can be removed from the polyimide-based resin membrane by being decomposed into monomers, low molecular weight substances, or CO₂ in a case of being heated.

[0057]

 Among the depolymerizable polymers, from the viewpoint of handling at the
15 time of pore formation, a polymer of methyl methacrylate or isobutyl methacrylate alone (a polymethyl methacrylate or a polyisobutyl methacrylate), which has a low thermal decomposition temperature, or a copolymerization polymer containing this as a main component is preferable.

[0058]

20 The decomposition temperature of the resin fine particles is preferably in a range of 200°C to 320°C and more preferably in a range of 230°C to 260°C. In a case where the decomposition temperature is 200°C or higher, membrane formation can be carried out even in a case where a high boiling point solvent is used for the varnish, and the range of selection of sintering conditions for the polyimide-based resin becomes wider.
25 In a case where the decomposition temperature is 320°C or lower, only the resin fine

particles can be easily eliminated without causing thermal damage to the polyimide-based resin.

[0059]

The fine particles preferably have a high true sphere ratio since they tend to have
5 a curved surface on the inner surface of the pore in the formed porous membrane. The particle diameter (average diameter) of the fine particles to be used is, for example, preferably in a range of 15 to 1,000 nm and more preferably in a range of 20 to 400 nm.

In a case where the average diameter of the fine particles is within the above range, a filtration target can be brought into uniform contact with the inner surface of the
10 pores in the porous membrane in a case where the filtration target is allowed to pass through the polyimide-based resin porous membrane obtained by removing the fine particles, and thus foreign substances contained in the filtration target can be efficiently adsorbed.

[0060]

15 The particle diameter distribution index (d_{25}/d_{75}) of the fine particles is preferably in a range of 1 to 6 and more preferably in a range of 1.6 to 5, and still more preferably in a range of 2 to 4.

In a case where the particle diameter distribution index is set equal to or larger than the preferred lower limit value of the above range, the inside of the porous
20 membrane can be efficiently filled with fine particles, and thus a flow path is easily formed, and the flow rate is improved. In addition, pores having different sizes are easily formed, different kinds of convection are generated, and thus the adsorption rate of foreign substances is further improved.

It is noted that d_{25} and d_{75} are values of particle diameters in which the
25 cumulative frequencies of the particle size distribution are each 25% and 75%, and d_{25} is

the value having the larger particle diameter in the present specification.

[0061]

In addition, in a case of forming an unsintered composite membrane in a two-layer shape in [Membrane formation of unsintered composite membrane] described later, as a fine particle (B1) that is used for a first varnish and a fine particle (B2) that is used for a second varnish, the same one may be used or those different from each other may be used. In order to make the pores on the side in contact with the base material more dense, it is preferable that the fine particle (B1) has a small or the same particle diameter distribution index as compared with the fine particle (B2). Alternatively, it is preferable that the fine particle (B1) has a small or the same true sphere ratio as compared with the fine particle (B2). In addition, the fine particle (B1) preferably has a smaller particle diameter (average diameter) than the fine particle (B2), and in particular, it is preferable that the fine particle (B1) in a range of 100 to 1,000 nm (more preferably in a range of 100 to 600 nm) and the fine particle (B2) in a range of 500 to 2,000 nm (more preferably in a range of 700 to 2,000 nm) are each used. In a case where fine particle (B1) having a particle diameter smaller than that of the fine particles (B2) is used, the opening proportion of the pores on the surface of the polyimide-based resin porous membrane to be obtained can be increased, and the diameters thereof can be made uniform, and the strength of the porous membrane can be increased as compared with a case where the entire polyimide-based resin porous membrane is made of the fine particle (B1) alone.

[0062]

In the present embodiment, a dispersing agent may be further added to the varnish together with the fine particles for the intended purpose of uniformly dispersing the fine particles. In a case of further adding a dispersing agent, it is possible to more uniformly mix polyamic acid, or polyimide or polyamide-imide with fine particles, and

in addition, it is possible to more uniformly distribute the fine particles in the unsintered composite membrane. As a result of the above, it is possible to efficiently form an interconnection pore that is allowed to be connected to the front and back surfaces of the polyimide-based resin porous membrane, and thus dense openings are provided on the surface of the polyimide-based resin porous membrane to be finally obtained and the air permeability of the polyimide-based resin porous membrane is improved.

[0063]

As the dispersing agent, a publicly known dispersing agent can be used without particular limitation. Examples of the dispersing agent include anionic surfactants such as a palm fatty acid salt, a castor sulfate oil salt, a lauryl sulfate salt, a polyoxyalkylene allylphenyl ether sulfate salt, an alkylbenzene sulfonic acid, an alkylbenzene sulfonic acid salt, an alkyldiphenyl ether disulfonic acid salt, an alkylnaphthalene sulfonic acid salt, a dialkyl sulfosuccinate salt, isopropyl phosphate, a polyoxyethylene alkyl ether phosphate salt, and a polyoxyethylene allylphenyl ether phosphate salt; cationic surfactants such as an oleylamine acetic acid salt, laurylpyridinium chloride, cetylpyridinium chloride, lauryltrimethylammonium chloride, stearyltrimethylammonium chloride, behenyltrimethylammonium chloride, and didecyldimethylammonium chloride; amphoteric surfactants such as a palm alkyldimethylamine oxide, a fatty acid amide propyldimethylamine oxide, an alkylpolyaminoethylglycine hydrochloric acid salt, an amide betaine-type activator, an alanine-type activator, and lauryliminodipropionic acid; polyoxyalkylene primary alkyl ether-based or polyoxyalkylene secondary alkyl ether-based nonionic surfactants such as a polyoxyethylene octyl ether, a polyoxyethylene decyl ether, a polyoxyethylene lauryl ether, a polyoxyethylene laurylamine, a polyoxyethylene oleylamine, a polyoxyethylene polystyrylphenyl ether, and a polyoxyalkylene polystyrylphenyl ether, and polyoxyalkylene-based nonionic surfactants

such as a polyoxyethylene dilaurate, a polyoxyethylene laurate, a polyoxyethylenated castor oil, a polyoxyethylenated hydrogenated castor oil, a sorbitan lauric acid ester, a polyoxyethylene sorbitan lauric acid ester, and a fatty acid diethanol amide; fatty acid alkyl esters such as octyl stearate and trimethylolpropane tridecanoate; and polyether

5 polyols such as a polyoxyalkylene butyl ether, a polyoxyalkylene oleyl ether, and trimethylolpropane tris(polyoxyalkylene) ether. The above dispersing agent can be used alone, or two or more thereof can be mixed and used.

[0064]

... Polyamic acid

10 Examples of the polyamic acid that can be used in the present embodiment include those obtained by polymerizing any tetracarboxylic acid dianhydride with a diamine.

[0065]

.... Tetracarboxylic acid dianhydride

15 The tetracarboxylic acid dianhydride can be appropriately selected from the tetracarboxylic acid dianhydrides that are used as raw materials for synthesizing polyamic acids in the related art.

The tetracarboxylic acid dianhydride may be an aromatic tetracarboxylic acid dianhydride or may be an aliphatic tetracarboxylic acid dianhydride.

20 [0066]

Examples of the aromatic tetracarboxylic acid dianhydride include pyromellitic acid dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic acid

25 dianhydride, 2,2,6,6-biphenyltetracarboxylic acid dianhydride, 2,2-bis(3,4-

dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, bis(3,4-dicarboxyphenyl)ether dianhydride, bis(2,3-dicarboxyphenyl)ether dianhydride, 2,2',3,3'-benzophenonetetracarboxylic acid dianhydride, 4,4-(p-phenylenedioxy)diphthalic acid dianhydride, 4,4-(m-phenylenedioxy)diphthalic acid dianhydride, 1,2,5,6-naphthalenetetracarboxylic acid dianhydride, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 1,2,3,4-benzenetetracarboxylic acid dianhydride, 3,4,9,10-perylenetetracarboxylic acid dianhydride, 2,3,6,7-anthracenetetracarboxylic acid dianhydride, 1,2,7,8-phenanthrenetetracarboxylic acid dianhydride, 9,9-bis phthalic acid anhydride fluorene, and 3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride.

[0067]

15 Examples of the aliphatic tetracarboxylic acid dianhydride include ethylenetetracarboxylic acid dianhydride, butanetetracarboxylic acid dianhydride, cyclopentanetetracarboxylic acid dianhydride, cyclohexanetetracarboxylic acid dianhydride, 1,2,4,5-cyclohexanetetracarboxylic acid dianhydride, and 1,2,3,4-cyclohexanetetracarboxylic acid dianhydride.

20 [0068]

Among the above, an aromatic tetracarboxylic acid dianhydride is preferable from the viewpoint of heat resistance of the polyimide resin to be obtained. Among them, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride or pyromellitic acid dianhydride is preferable from the viewpoint of price, availability.

25 The tetracarboxylic acid dianhydride may be used alone, or two or more thereof

can be mixed and used.

[0069]

.... Diamine

A diamine can be appropriately selected from the diamines that are used as raw materials for synthesizing polyamic acids in the related art. This diamine may be an aromatic diamine or an aliphatic diamine; however, an aromatic diamine is preferable from the viewpoint of heat resistance of the polyimide resin to be obtained. The diamine can be used alone, or two or more thereof can be mixed and used.

[0070]

Examples of the aromatic diamine include a diamino compound obtained by bonding one phenyl group or about 2 to 10 phenyl groups. Specific examples of the aromatic diamine include a phenylene diamine or a derivative thereof, a diaminobiphenyl compound or a derivative thereof, a diaminodiphenyl compound or a derivative thereof, a diaminotriphenyl compound or a derivative thereof, a diaminonaphthalene or a derivative thereof, an aminophenyl aminoindane or a derivative thereof, a diaminotetraphenyl compound or a derivative thereof, a diaminohexaphenyl compound or a derivative thereof, and a cardo-type fluorene diamine derivative.

[0071]

The phenylene diamine is preferably m-phenylene diamine or p-phenylene diamine. Examples of the phenylene diamine derivative include diamines to which an alkyl group such as a methyl group or an ethyl group is bonded, for example, 2,4-diaminotoluene and 2,4-triphenylenediamine.

[0072]

The diaminobiphenyl compound is a compound in which two aminophenyl groups are bonded by the bonding of phenyl groups to each other. Examples of the

diaminobiphenyl compound include 4,4'-diaminobiphenyl, and 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl.

[0073]

The diaminodiphenyl compound is a compound in which two aminophenyl
 5 groups are bonded through another group by the bonding of phenyl groups to each other. Examples of the other group include an ether bond, a sulfonyl bond, a thioether bond, an alkylene group or a derivative group thereof, an imino bond, an azo bond, a phosphine oxide bond, an amide bond, and a ureylene bond. The alkylene group preferably has about 1 to 6 carbon atoms, and the derivative group thereof is a group in which one or
 10 more hydrogen atoms of an alkylene group are substituted with a halogen atom or the like.

[0074]

Examples of the diaminodiphenyl compound include 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl
 15 sulfone, 3,4'-diaminodiphenyl sulfone, 4, 4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl methane, 3,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl sulfide, 3,3'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 2,2-bis(p-aminophenyl)propane, 2,2'-bis(p-aminophenyl)hexafluoropropane, 4-methyl-2,4-bis(p-aminophenyl)-1-pentene, 4-methyl-
 20 2,4-bis(p-aminophenyl)-2-pentene, iminodianiline, 4-methyl-2,4-bis(p-aminophenyl)pentane, bis(p-aminophenyl)phosphine oxide, 4,4'-diaminoazobenzene, 4,4'-diaminodiphenyl urea, 4,4'-diaminodiphenyl amide, 1,4-bis(4-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 4,4'-bis(4-aminophenoxy)biphenyl, bis[4-(4-
 25 aminophenoxy)phenyl] sulfone, bis[4-(3-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-

aminophenoxy)phenyl]propane, and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane.

[0075]

The diaminotriphenyl compound is a compound obtained by bonding each of
 5 two aminophenyl groups and one phenylene group through another group. Examples of the other group include the same one as the other group in diaminodiphenyl compound.

Examples of the diaminotriphenyl compound include 1,3-bis(m-aminophenoxy)benzene, 1,3-bis(p-aminophenoxy)benzene, and 1,4-bis(p-aminophenoxy)benzene.

10 [0076]

Examples of diaminonaphthalene include 1,5-diaminonaphthalene and 2,6-diaminonaphthalene.

[0077]

Examples of aminophenyl aminoindane include 5- or 6-amino-1-(p-aminophenyl)-1,3,3-trimethylindane.
 15

[0078]

Examples of the diaminotetraphenyl compound include 4,4'-bis(p-aminophenoxy)biphenyl, 2,2'-bis[p-(p'-aminophenoxy)phenyl]propane, 2,2'-bis[p-(p'-aminophenoxy)biphenyl]propane, and 2,2'-bis[p-(m-aminophenoxy)phenyl]benzophenone.
 20

[0079]

Examples of the cardo-type fluorene diamine derivative include 9,9-bis aniline fluorene.

[0080]

25 The aliphatic diamine preferably has, for example, about 2 to 15 carbon atoms,

and specific examples thereof include pentamethylenediamine, hexamethylenediamine, and heptamethylenediamine.

[0081]

Here, the diamine may be a compound in which a hydrogen atom is substituted
5 with at least one kind of substituent selected from the group consisting of a halogen atom, a methyl group, a methoxy group, a cyano group, and a phenyl group.

[0082]

Among the above, the diamine is preferably a phenylene diamine, a phenylene
diamine derivative, or a diaminodiphenyl compound. Among them, p-phenylene
10 diamine, m-phenylene diamine, 2,4-diaminotoluene, or 4,4'-diaminodiphenyl ether is particularly preferable from the viewpoint of price, availability.

[0083]

The manufacturing method for a polyamic acid is not particularly limited, and a
publicly known technique such as a method of reacting any tetracarboxylic acid
15 dianhydride with a diamine in an organic solvent is used.

The reaction of tetracarboxylic acid dianhydride with a diamine is generally
carried out in an organic solvent. The organic solvent used here is not particularly
limited as long as it can dissolve each of tetracarboxylic acid dianhydride and a diamine
and does not react with tetracarboxylic acid dianhydride and a diamine. The organic
20 solvent can be used alone, or two or more thereof can be mixed and used.

[0084]

Examples of the organic solvent that is used for the reaction between
tetracarboxylic acid dianhydride and a diamine include nitrogen-containing polar
solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-
25 diethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, N-

methylocaprolactam, N,N,N',N'-tetramethyl urea; lactone-based polar solvents such as β -propiolactone, γ -butyrolactone, γ -valerolactone, δ -valerolactone, γ -caprolactone, and ϵ -caprolactone; dimethylsulfoxide; acetonitrile; fatty acid esters such as ethyl lactate and butyl lactate; ethers such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, dioxane, tetrahydrofuran, methyl cellosolve acetate, and ethyl cellosolve acetate; and phenol-based solvents such as cresols.

[0085]

Among these, as the organic solvent here, it is preferable to use a nitrogen-containing polar solvent from the viewpoint of the solubility of the polyamic acid to be generated.

In addition, from the viewpoint of membrane formation property and the like, it is preferable to use a mixed solvent containing a lactone-based polar solvent. In this case, the content of the lactone-based polar solvent is preferably in a range of 1% to 20% by mass and more preferably in a range of 5% to 15% by mass with respect to the entire organic solvent (100% by mass).

As the organic solvent here, it is preferable to use one or more selected from the group consisting of a nitrogen-containing polar solvent and a lactone-based polar solvent, and it is more preferable to use a mixed solvent of a nitrogen-containing polar solvent and a lactone-based polar solvent.

The using amount of the organic solvent is not particularly limited; however, it is preferably such an amount that the content of the generated polyamic acid in the reaction solution after the reaction is in a range of 5% to 50% by mass.

[0086]

The using amount of each of tetracarboxylic acid dianhydride and a diamine used is not particularly limited; however, it is preferable to use an amount in a range of

0.50 to 1.50 mol, more preferable to use an amount in a range of 0.60 to 1.30 mol, and particularly preferable to use an amount in a range of 0.70 to 1.20 mol, with respect to the 1 mol of tetracarboxylic acid dianhydride.

[0087]

- 5 The reaction (polymerization) temperature is generally in a range of -10°C to 120°C and preferably in a range of 5°C to 30°C.

 The reaction (polymerization) time varies depending on the raw material composition to be used; however, it is generally in a range of 3 to 24 (hours).

- The intrinsic viscosity of the polyamic acid solution obtained under such
10 conditions is preferably in a range of 1,000 to 100,000 centipoise (cP) (1 to 100 Pa·s) and more preferably 5,000 to 70,000 cP (5 to 70 Pa·s).

 The intrinsic viscosity of the polyamic acid solution can be measured with an E-type rotational viscometer under a temperature condition of 25°C.

[0088]

- 15 ... Polyimide

 As the polyimide that can be used in the present embodiment, any publicly known polyimide can be used as long as it can be dissolved in an organic solvent that is used for the varnish, without being limited by the structure and the molecular weight thereof.

- 20 The polyimide may have, in the side chain, a condensable functional group such as a carboxy group or a functional group that promotes a crosslinking reaction or the like during sintering.

[0089]

- In order to obtain polyimide that is soluble in an organic solvent that is used for
25 the varnish, it is effective to use a monomer for introducing a flexible bent structure into

the main chain.

Examples of this monomer include aliphatic diamines such as ethylenediamine, hexamethylenediamine, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, and 4,4'-diaminodicyclohexylmethane; aromatic diamines such as 2-methyl-1,4-phenylenediamine, o-tolidine, m-tolidine, 3,3'-dimethoxybenzidine, and 4,4'-diaminobenzanilide; polyoxyalkylenediamines such as polyoxyethylenediamine, polyoxypropylenediamine, and polyoxybutylenediamine; polysiloxanediamine; 2,3,3',4'-oxydiphthalic acid anhydride, 3,4,3',4'-oxydiphthalic acid anhydride, and 2,2-bis(4-hydroxyphenyl)propanedibenzoate-3,3',4,4'-tetracarboxylic acid dianhydride.

10 [0090]

In addition, it is also effective to use a monomer having a functional group that improves the solubility in such an organic solvent. Examples of the monomer having such a functional group include fluorinated diamines such as 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 2-trifluoromethyl-1,4-phenylenediamine.

15 Further, in addition to the monomer having such a functional group, the monomer described as an example in the above description of the polyamic acid can be used in combination as long as the solubility is not impaired.

[0091]

20 The manufacturing method for polyimide is not particularly limited, and examples thereof include a publicly known technique such as a method in which polyamic acid is chemically imidized or thermally imidized to be dissolved in an organic solvent.

[0092]

25 Examples of the polyimide that can be used in the present embodiment include an aliphatic polyimide (a full-aliphatic polyimide) and an aromatic polyimide, and among

them, an aromatic polyimide is preferable.

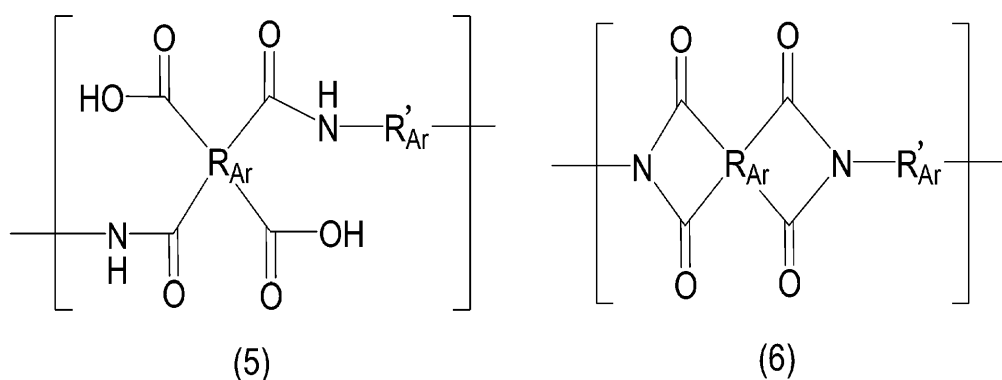
The aromatic polyimide may be one obtained by subjecting a polyamic acid having a constitutional unit represented by General Formula (5) to thermal or chemical ring-closure reaction or may be one obtained by dissolving a polyimide having a

5 constitutional unit represented by General Formula (6) in a solvent.

In the formula, R_{Ar} represents an aryl group, and R'_{Ar} represents an arylene group.

[0093]

[Chemical Formula 3]



10

[0094]

In the above formula, R_{Ar} is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic.

The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon

15 atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12

carbon atoms. Specifically, as the aromatic ring, an aromatic hydrocarbon ring such as benzene, naphthalene, anthracene, and phenanthrene; and an aromatic heterocyclic ring in which a part of carbon atoms constituting the aromatic hydrocarbon ring have been substituted with heteroatoms are exemplary examples. Examples of the hetero atom in

20 the aromatic heterocyclic rings include an oxygen atom, a sulfur atom, and a nitrogen

atom. Specific examples of the aromatic heterocyclic ring include a pyridine ring and a thiophene ring. Among them, R_{Ar} is preferably an aromatic hydrocarbon ring, more preferably benzene or naphthalene, and particularly preferably benzene.

In the above formula, examples of R'_{Ar} include the group obtained by removing two hydrogen atoms from the aromatic ring R_{Ar} described above. Among them, R'_{Ar} is preferably a group obtained by removing two hydrogen atoms from an aromatic hydrocarbon ring, more preferably a group obtained by removing two hydrogen atoms from benzene or naphthalene, and particularly preferably a phenylene group obtained by removing two hydrogen atoms from benzene.

The aryl group in R_{Ar} and the arylene group in R'_{Ar} may each have a substituent.
[0095]

... Polyamide-imide

As the polyamide-imide that can be used in the present embodiment, any publicly known polyamide-imide can be used as long as it can be dissolved in an organic solvent that is used for the varnish, without being limited by the structure and the molecular weight thereof.

The polyamide-imide may have, in the side chain, a condensable functional group such as a carboxy group or a functional group that promotes a crosslinking reaction or the like during sintering.

[0096]

As such a polyamide-imide, it is possible to use, without particular limitation, one obtained by reacting any trimellitic acid anhydride with a diisocyanate or one obtained by imidizing a precursor polymer that is obtained by reacting a reactive derivative of any trimellitic acid anhydride with a diamine.

[0097]

Examples of the reactive derivative of any trimellitic acid anhydride include a halogenated trimellitic acid anhydride such as trimellitic anhydride chloride and a trimellitic acid anhydride ester.

[0098]

- 5 Examples of any diisocyanate include metaphenylene diisocyanate, p-phenylene diisocyanate, o-tolidine diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 4,4'-oxybis(phenyl isocyanate), 4,4'-diisocyanate diphenylmethane, bis[4-(4-isocyanatophenoxy)phenyl]sulfone, 2,2'-bis[4-(4-isocyanatophenoxy)phenyl]propane, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 10 3,3'-dimethyldiphenyl-4,4'-diisocyanate, 3,3'-diethyldiphenyl-4,4'-diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, m-xylene diisocyanate, p-xylene diisocyanate, and naphthalene diisocyanate.

[0099]

- 15 Examples of any diamine include the same ones as the diamines described as an example in the description of the polyamic acid described above.

[0100]

... Organic solvent

- 20 The organic solvent that can be used for preparing the varnish is not particularly limited as long as it can dissolve the polyamic acid and/or the polyimide-based resin and does not dissolve fine particles, and examples thereof include the same one as the organic solvent that is used in the reaction between tetracarboxylic acid dianhydride and a diamine.

- 25 The organic solvent can be used alone, or two or more thereof can be mixed and used.

[0101]

The content of the organic solvent in the varnish is preferably in a range of 50% to 95% by mass and more preferably in a range of 60% to 85% by mass. The solid content concentration in the varnish is preferably in a range of 5% to 50% by mass and
5 more preferably in a range of 15% to 40% by mass.

[0102]

In addition, in a case of forming an unsintered composite membrane in a two-layer shape in the [Membrane formation of unsintered composite membrane] described later, the volume ratio of polyamic acid or polyimide, or a polyamide-imide (A1) to a
10 fine particle (B1) in the first varnish is preferably set in a range of 19:81 to 45:55. In a case where the total volume is assumed to be 100, particles are uniformly dispersed in a case where proportion of the volume occupied by the fine particle (B1) is 55 or more, and particles are easily dispersed without being aggregated in a case where it is 81 or less. This makes it possible to uniformly form pores on the surface side of the base material of
15 the polyimide-based resin molded membrane.

In addition, the volume ratio of polyamic acid or polyimide, or a polyamide-imide (A2) to a fine particle (B2) in the second varnish is preferably set in a range of 20:80 to 50:50. In a case where the total volume is assumed to be 100, simple bodies of particles are easily dispersed uniformly in a case where the proportion of the volume
20 occupied by the fine particle (B2) is 50 or more, and particles are not aggregated and surface cracking or the like hardly occurs in a case where it is 80 or less. As a result, a polyimide-based resin porous membrane having good mechanical characteristics such as stress and breaking elongation is easily formed.

[0103]

25 In regard to the above volume ratio, it is preferable that the second varnish has a

lower fine particle content rate than the first varnish. In a case where the above conditions are satisfied, the strength and flexibility of the unsintered composite membrane, the polyimide-based resin-fine particle composite membrane, and the polyimide-based resin porous membrane are ensured even in a case where polyamic acid or polyimide, or polyamide-imide is filled with fine particles to a high degree. In addition, in a case where a layer having a low fine particle content rate is provided, the manufacturing cost can be reduced.

[0104]

In a case of preparing a varnish, in addition to the above-described components, it is possible to blend, as necessary, publicly known components such as an antistatic agent, a flame retardant, a chemical imidizing agent, a condensing agent, a mold releasing agent, and a surface conditioner for the intended purpose of prevention of static charge, flame retardancy impartment, low temperature sintering, mold releasability, coatability.

[0105]

[Membrane formation of unsintered composite membrane]

The membrane formation of the unsintered composite membrane containing polyamic acid or polyimide, or polyamide-imide and containing fine particles is carried out, for example, by coating a base material with the above varnish and drying under the conditions of normal pressure or vacuum at a temperature in a range of 0°C to 120°C (preferably 0°C to 100°C) and more preferably under the conditions of normal pressure at a temperature in a range of 60°C to 95°C (still more preferably 65°C to 90°C). The coating film thickness is, for example, preferably 1 to 500 μm and more preferably 5 to 50 μm .

[0106]

Here, a mold releasing layer may be provided on the base material as necessary. In addition, in the membrane formation of the unsintered composite membrane, each of a dipping step of carrying out dipping in a solvent containing water, a drying step, and a pressing step may be provided as optional steps before [Sintering of unsintered
5 composite membrane] described later.
[0107]

The mold releasing layer can be prepared by applying a mold releasing agent on the base material and carrying out drying or baking. As the mold releasing agent used here, a publicly known mold releasing agent such as an alkyl phosphate ammonium salt-
10 based mold releasing agent, a fluorine-based mold releasing agent, or a silicone-based mold releasing agent can be used without particular limitation.

In a case where the unsintered composite membrane after drying is peeled from the base material, a small amount of the mold releasing agent remains on the peeled surface of the unsintered composite membrane. Since the remaining mold releasing
15 agent may affect the wettability of the surface of the polyimide-based resin porous membrane and the mixing of impurities, it is preferable to remove the remaining mold releasing agent.

As a result, it is preferable to wash the unsintered composite membrane peeled from the base material with an organic solvent or the like. Examples of the washing
20 method include a publicly known technique such as a method of dipping an unsintered composite membrane in a washing liquid and then taking it out and a method of shower washing.

In order to dry the unsintered composite membrane after washing, for example, the unsintered composite membrane after washing is air-dried at room temperature or
25 heated to a suitable set temperature in a constant temperature bath. In that case, for

example, it is possible to adopt a method in which an end part of the unsintered composite membrane is fixed to a mold made of SUS or the like to prevent deformation.

[0108]

On the other hand, in a case where the base material is used as it is without providing a mold releasing layer in the membrane formation of the unsintered composite membrane, the step of forming the mold releasing layer and the step of washing the unsintered composite membrane can be omitted.

[0109]

In addition, in a case where the unsintered composite membrane is formed into a membrane in a two-layer shape, first, the formation of a first unsintered composite membrane having a membrane thickness in a range of 1 to 5 μm is carried out by directly coating a base material such as glass plate with the above first varnish and then drying under the conditions of normal pressure or vacuum at a temperature in a range of 0°C to 120°C (preferably 0°C to 90°C) and more preferably under the conditions of normal pressure at a temperature in a range of 10°C to 100°C (still more preferably 10°C to 90°C).

Subsequently, the first unsintered composite membrane is coated with the above second varnish, and drying is carried out in the same manner under the conditions of a temperature in a range of 0°C to 80°C (preferably 0°C to 50°C) and more preferably under the conditions of normal pressure at a temperature in a range of 10°C to 80°C (still more preferably 10°C to 30°C) to form a second unsintered composite membrane having a membrane thickness in a range of 5 to 50 μm , whereby unsintered composite membrane having a two-layer shape can be formed into a membrane.

[0110]

[Sintering of unsintered composite membrane]

After [Membrane formation of unsintered composite membrane] described above, the unsintered composite membrane is subjected to a heating treatment (sintering) to form a composite membrane (a polyimide-based resin-fine particle composite membrane) consisting of a polyimide-based resin and fine particles.

5 In a case where the varnish contains polyamic acid, it is preferable to complete the imidization by [Sintering of unsintered composite membrane] of the present step.
[0111]

 The temperature (the sintering temperature) of the heating treatment varies depending on the structure of the polyamic acid, or polyimide or polyamide-imide
10 contained in the unsintered composite membrane and the presence or absence of the condensing agent; however, it is preferably in a range of 120°C to 400°C and more preferably in a range of 150°C to 375°C.
[0112]

 For carrying out sintering, it is not always necessary to clearly separate the
15 operation from the drying in the previous step. For example, in a case of carrying out sintering at 375°C, it is possible to use a method in which the temperature is raised from room temperature to 375°C in 3 hours and then held at 375°C for 20 minutes, or a stepwise drying-thermal imidization method in which the temperature is gradually raised from room temperature to 375°C in 50°C increments (held for 20 minutes in each
20 increment) and finally held at 375°C for 20 minutes. In that case, a method in which an end part of the unsintered composite membrane is fixed to a mold made of SUS or the like may be adopted to prevent deformation.
[0113]

 The thickness of the polyimide-based resin-fine particle composite membrane
25 after the heating treatment (sintering) is, for example, preferably 1 μm or more, more

preferably in a range of 5 to 500 μm , and still more preferably in a range of 8 to 100 μm .

The thickness of the polyimide-based resin-fine particle composite membrane can be determined by measuring thicknesses of a plurality of positions using a micrometer and averaging the measured thicknesses.

5 [0114]

The present step is an optional step. The present step may not be carried out, particularly in a case where polyimide or polyamide-imide is used for the varnish.

[0115]

[Fine particle removal]

10 After [Sintering of unsintered composite membrane] described above, the fine particles are removed from the polyimide-based resin-fine particle composite membrane, whereby a polyimide-based resin porous membrane is manufactured.

For example, in a case where silica is employed as the fine particle, the polyimide-based resin-fine particle composite membrane is brought into contact with a
 15 low-concentration hydrogen fluoride (HF) water to dissolve and remove the silica, whereby a porous membrane is obtained. In addition, in a case where the fine particles are resin fine particles, the resin fine particles are decomposed and removed by heating to a temperature equal to or higher than thermal decomposition temperature of the resin fine particles and lower than thermal decomposition temperature of the polyimide-based
 20 resin, whereby a porous membrane is obtained.

[0116]

[Etching (decyclization of imide bond)]

The etching step can be carried out by a chemical etching method or a physical removal method, or by a method in which these methods are combined.

25 [0117]

· In regard to chemical etching method

A publicly known method in the related art can be used as the chemical etching method.

The chemical etching method is not particularly limited, and examples thereof
5 include a treatment with an etching liquid such as an inorganic alkaline solution or an organic alkaline solution. Among the above, a treatment with an inorganic alkaline solution is preferable.

Examples of the inorganic alkaline solution include a hydrazine solution containing hydrazine hydrate and ethylenediamine; a solution of an alkali metal
10 hydroxide such as potassium hydroxide, sodium hydroxide, sodium carbonate, sodium silicate, or sodium metasilicate; an ammonia solution; and an etching liquid containing alkali hydroxide, hydrazine, and 1,3-dimethyl-2-imidazolidinone as main components.

Examples of the organic alkaline solution include primary amines such as ethyl amine and n-propyl amine; secondary amines such as diethyl amine and di-n-butyl
15 amine; tertiary amines such as triethyl amine and methyldiethyl amine; alcohol amines such as dimethylethanol amine and triethanol amine; quaternary ammonium salts such as tetramethylammonium hydroxide and tetraethylammonium hydroxide; and alkaline etching liquids such as cyclic amines such as pyrrole and piperidine. The alkali concentration in the etching liquid is, for example, in a range of 0.01% to 20% by mass.

20 [0118]

Pure water or alcohols can be appropriately selected as the solvent for each of the above etching liquids, and those to which a suitable amount of a surfactant is added can also be used.

[0119]

25 · In regard to physical removal method

As the physical removal method, for example, a dry etching method using plasma (oxygen, argon, or the like), corona discharge, or the like can be used.

[0120]

The above-described chemical etching method or physical removal method can be applied before [Fine particle removal] described above or can be applied after [Fine particle removal] described above.

Among the above, it is preferable to be applied after [Fine particle removal] described above since the interconnection pores inside the polyimide-based resin porous membrane are more easily formed and the foreign substance removability is enhanced.

10 [0121]

In a case where the chemical etching method is carried out in the etching step, a step of washing the polyimide-based resin porous membrane may be provided after the present step in order to remove excess etching liquid.

The washing after the chemical etching may be carried out by washing with water alone; however, it is preferable to combine washing with acid and washing with water.

[0122]

In addition, after the etching step, the polyimide-based resin porous membrane may be subjected to a heating treatment (re-sintering) in order to improve the wettability of the polyimide-based resin porous membrane surface to an organic solvent and remove residual organic substances. The conditions of this heating are the same as the conditions in [Sintering of unsintered composite membrane] described above.

[0123]

For example, in the polyimide-based resin porous membrane manufactured by the above-described manufacturing method, spherical cells and an interconnection pore

in which adjacent spherical cells are connected to each other are formed. The polyimide-based resin porous membrane preferably has an interconnection pore so that an interconnection pore that opens on one outer surface is connected to the inside of the porous membrane and opens up to the other (on the back side) outer surface, and thus a flow path in which a fluid can pass through the porous membrane is ensured.

[0124]

The Garley air permeability of the "porous membrane in which adjacent spherical cells are connected to each other" is, for example, preferably 30 seconds or more from the viewpoint of efficiently removing foreign substances while maintaining a certain degree of high flow rate of a filtration target that passes through the porous membrane. The Garley air permeability of the porous membrane is more preferably in a range of 30 to 1,000 seconds, still more preferably in a range of 30 to 600 seconds, particularly preferably in a range of 30 to 500 seconds, and most preferably in a range of 30 to 300 seconds. In a case where the Garley air permeability is equal to or smaller than the preferred upper limit value of the above range, the degree of porosity (the presence ratio of the interconnection pore and the like) is sufficiently high, and thus the effect of removing foreign substances can be more easily obtained.

The Garley air permeability of the porous membrane can be measured according to JIS P 8117.

[0125]

The "porous membrane in which adjacent spherical cells are connected to each other" preferably contains interconnection pores having an average pore diameter (average pore diameter of porous membrane) in a range of 1 to 1,000 nm, more preferably in a range of 3 to 300 nm, still more preferably in a range of 5 to 100 nm, and particularly preferably in a range of 10 to 40 nm. Any combination of the upper limit

value and the lower limit value may be allowed, and for example, the average pore diameter of the porous membrane may be 10 to 1,000 nm.

The pore diameter of the interconnection pore means the diameter of the interconnection pore. However, for example, in a case where a direction in which two pores constituting an interconnection pore are adjacent to each other is denoted by a longitudinal direction, a direction perpendicular to the longitudinal direction is included in the above diameter since one interconnection pore is generally formed from two adjacent particles by the above-described manufacturing method. In a case where the above-described etching (the decyclization of the imide bond) step is not provided, the pore diameter of the interconnection pore tends to be small.

The average pore diameter of the interconnection pores in the porous membrane (also referred to as the average pore diameter of the porous membrane) is a value measured using a Perm Porometer (for example, manufactured by Porous Materials Inc.) according to the half-dry method (ASTM E1294-89) using perfluoropolyester (product name: Galwick, interfacial tension value: 15.9 dyne/cm) as the test liquid at a measurement temperature of 25°C and a measurement pressure range of 0 to 400 psi.

[0126]

The average pore diameter of the spherical cells of "the porous membrane in which adjacent spherical cells are connected to each other" is preferably in a range of 20 to 2,500 nm, more preferably in a range of 30 to 1,000 nm, and still more preferably in a range of 50 to 250 nm.

[0127]

As described above, the "porous membrane in which adjacent spherical cells are connected to each other" is preferably a porous membrane containing pores having an average pore diameter of several hundred nanometers. As a result, for example, even

minute substances in the nanometer unit can be adsorbed to or captured in the pores and/or the interconnection pores in the porous membrane.

[0128]

Regarding the pore diameter of the interconnection pore, in a case where the
5 distribution of the pore diameters of the individual pores that impart porosity to the "porous membrane in which adjacent spherical cells are connected to each other" is broader, the pore diameter of the interconnection pore that is formed by pores adjacent to each other tends to be smaller.

From the viewpoint of reducing the pore diameter of the interconnection pores,
10 the void ratio of the "porous membrane in which adjacent spherical cells are connected to each other" is, for example, preferably 50% by mass or greater, more preferably in a range of 55% to 90% by mass, still more preferably in a range of 60% to 80% by mass, and particularly preferably in a range of about 60% to 70% by mass. In a case where the void ratio is equal to or larger than the above-described preferred lower limit value of
15 the above-described range, the effect of removing foreign substances can be more easily obtained. In a case where it is equal to or smaller than the preferred upper limit value of the above range, the strength of the porous membrane is further increased.

The void ratio of the porous membrane is determined by calculating the proportion of the mass of the fine particles with respect to the total mass of the resin and
20 the like that are used in the manufacturing of the porous membrane, and the fine particles.

[0129]

The "porous membrane in which adjacent spherical cells are connected to each other" is excellent in mechanical characteristics such as stress and breaking elongation.

25 The stress of the "porous membrane in which adjacent spherical cells are

connected to each other" provided in the filter is, for example, preferably 10 MPa or greater, more preferably 15 MPa or greater, and still more preferably in a range of 15 to 60 MPa.

5 The stress of the porous membrane is a value measured by preparing a sample having a size of 4 mm × 30 mm and subjecting the sample to the measurement using a testing machine under the measuring condition of 5 mm/min.

[0130]

In addition, the breaking elongation of the "porous membrane in which adjacent spherical cells are connected to each other" is, for example, preferably 10% GL or more and more preferably 15% GL or more. The upper limit of the breaking elongation is, 10 for example, preferably 60% GL or less and more preferably 55% GL or less. In a case where the void ratio of the polyimide-based resin porous membrane decreases, breaking elongation tends to increase.

The breaking elongation of the porous membrane is a value measured by 15 preparing a sample having a size of 4 mm × 30 mm and subjecting the sample to the measurement using a testing machine under the measuring condition of 5 mm/min.

[0131]

The thermal decomposition temperature of the "porous membrane in which adjacent spherical cells are connected to each other" is preferably 200°C or higher, more 20 preferably 320°C or higher, and still more preferably 350°C or higher.

The thermal decomposition temperature of the porous membrane can be measured by raising the temperature to 1,000°C at a temperature rising rate of 10 °C/min in an air atmosphere.

[0132]

25 The filter in the present embodiment is not limited to the one that includes a

porous membrane in which the interconnection pores 5 in which the adjacent spherical cell 1a and the spherical cell 1b are connected to each other as shown in FIG. 1 is formed, and may include a porous membrane in which, in addition to the interconnection pores 5, a cell or interconnection pore having another form is formed.

5 Examples of the cell (hereinafter, referred to as "another cell") having another form include a cell that differs in shape or pore diameter, and examples thereof include an elliptical cell, a polyhedral cell, and a spherical cell having a different pore diameter. Examples of the above-described "interconnection pore having another form" include an interconnection pore in which a spherical cell and another cell are connected to each
10 other.

 The shape or pore diameter of another cell may be appropriately determined depending on the kinds of impurities to be removed. The interconnection pore in which a spherical cell and another cell are connected to each other can be formed by the selection of material of the fine particle described above, the shape control of the fine
15 particles, and the like.

 According to the filter including a porous membrane in which, in addition to the interconnection pore in which adjacent spherical cells are connected to each other, a cell or interconnection pore having another form is formed, it is possible to efficiently remove various foreign substances from a filtration target.

20 [0133]

 In addition, the filter in the present embodiment can replace a filter cartridge or the like for removing impurities having a fine particle shape, which has been installed in the related art, in the supply lines of various chemical liquids or the point of use (POU) in the semiconductor manufacturing process or can be used in combination with these. As
25 a result, various foreign substances can be efficiently removed from a filtration target (a

chemical liquid for lithography) using the same device and operation as those in the related art, and a silicon-containing resin composition purified product having high purity can be prepared.

[0134]

5 <<Filtration of silicon-containing resin composition>>

Filtration of a silicon-containing resin composition using a filter having a porous structure in which adjacent spherical cells are connected to each other may be carried out in a state where differential pressure is not provided (that is, a silicon-containing resin composition may be allowed to pass through the filter only by gravity) or may be carried
10 out in a state where differential pressure is provided. Among the above, the latter is preferable, and it is preferable to carry out an operation of allowing a silicon-containing resin composition to pass through the filter by differential pressure.

[0135]

The phrase "state where differential pressure is provided" means that a pressure
15 difference is present between one side and the other side of the polyimide-based resin porous membrane provided in the filter.

For example, pressurization (positive pressure) that applies pressure to one side (the silicon-containing resin composition supply side) of the polyimide-based resin porous membrane, and decompression (negative pressure) that causes one side (the
20 filtrate side) of the polyimide-based resin porous membrane to be negative pressure are mentioned. In the filtration step according to the present embodiment, the former pressurization is preferable.

[0136]

The pressurization is an operation to apply pressure to the supply liquid side of
25 the polyimide-based resin porous membrane, where a silicon-containing resin

composition (hereinafter, may be referred to as a “supply liquid”) before being allowed to pass through the polyimide-based resin porous membrane is present on the supply liquid side.

For example, it is preferable to apply pressure to the supply liquid side by using the liquid flow pressure generated by the circulation or liquid feeding of the supply liquid or by using the positive pressure of the gas.

The liquid flow pressure can be generated, for example, by an active liquid flow pressure applying method with a pump (a feeding pump, a circulation pump, or the like). Examples of the pump include a rotary pump, a diaphragm pump, a metering pump, a chemical pump, a plunger pump, a bellows pump, a gear pump, a vacuum pump, an air pump, and a liquid pump.

In a case where the supply liquid is circulated or fed by the pump, the pump is generally arranged between the supply liquid bath (or the circulation bath) and the polyimide-based resin porous membrane.

[0137]

For example, in a case where a supply liquid is allowed to pass through the polyimide-based resin porous membrane only by gravity, the liquid flow pressure may be the pressure that is applied to the polyimide-based resin porous membrane by the supply liquid; however, it is preferably the pressure that is applied by the active liquid flow pressure applying method.

The gas that is used for pressurization is preferably a gas that is inert or non-reactive to the supply liquid, and specific examples thereof include nitrogen and a rare gas such as helium and argon.

Regarding a method of applying pressure to the supply liquid side, it is preferable to use the positive pressure of the gas. In that case, the filtrate side where the

filtrate has passed through the polyimide-based resin porous membrane may be at atmospheric pressure without being decompressed.

[0138]

In addition, the pressurization may utilize both the liquid flow pressure and the positive pressure of the gas. In addition, the differential pressure may be a combination of pressurization and decompression, and for example, one that utilizes both liquid flow pressure and decompression, one that utilizes both positive pressure and decompression of the gas, or one that utilizes liquid flow pressure, and positive pressure and decompression of the gas may be used. In a case where the method of providing differential pressure is combined, a combination of liquid flow pressure and positive pressure of the gas, or a combination of liquid flow pressure and decompression is preferable from the viewpoint of simplification of manufacturing.

In the present embodiment, as the method of providing differential pressure, for example, even one method using positive pressure by gas or the like is excellent in the performance of the foreign substance removal since the polyimide-based resin porous membrane is used.

[0139]

The decompression is an operation to decompress the filtrate side where the filtrate has passed through the polyimide-based resin porous membrane. For example, the decompression may be decompression by a pump; however, it is preferable to reduce pressure to form a vacuum.

[0140]

In a case where the operation of allowing the silicon-containing resin composition to pass through the filter is carried out in a state where differential pressure is provided, the pressure difference is appropriately set in consideration of the membrane

thickness, void ratio, or average pore diameter of the polyimide-based resin porous membrane to be used, or the desired degree of purification, the flow amount, the flow rate, or the concentration or viscosity of the supply liquid, or the like. For example, in a case of the so-called cross-flow method (the supply liquid is allowed to flow in parallel with the polyimide-based resin porous membrane), the pressure difference is preferably, for example, 0.3 MPa or less.

In a case of the so-called dead-end method (the supply liquid is allowed to flow to intersect the polyimide-based resin porous membrane), the pressure difference is, for example, preferably 1 MPa or less and more preferably 0.3 MPa or less. The lower limit value of each of the pressure differences is preferably 0.01 MPa or more and more preferably 0.05 MPa or more. Any combination of the upper limit value and the lower limit value may be allowed.

[0141]

In the step (i), the operation of allowing the silicon-containing resin composition to pass through the filter having the polyimide-based resin porous membrane described above can be carried out while maintaining a high flow rate of the silicon-containing resin composition (the supply liquid).

The flow rate in this case is not particularly limited; however, for example, the flow rate of pure water in a case of being pressurized at 0.08 MPa at room temperature (20°C) is preferably 1 mL/min or more, more preferably 3 mL/min or more, still more preferably 5 mL/min or more, and particularly preferably 10 mL/min or more. The upper limit value of the flow rate is not particularly limited, and it is, for example, 50 mL/min or less.

In the present embodiment, since the filter having the polyimide-based resin porous membrane described above is used, filtration can be carried out while maintaining

a high flow rate in this manner, and the removal rate of foreign substances contained in the silicon-containing resin composition can be increased.

[0142]

In addition, in the step (i), the operation of allowing the silicon-containing resin composition to pass through the filter is preferably carried out by setting the temperature of the silicon-containing resin composition in a range of 0°C to 30°C and more preferably carried out by setting in a range of 5°C to 25°C.

[0143]

In addition, in the step (i), the silicon-containing resin composition may be allowed to pass through the filter having the polyimide-based resin porous membrane a plurality of times (may be subjected to recirculation filtration a plurality of times) or may be allowed to pass through a plurality of filters including at least a filter having the polyimide-based resin porous membrane.

[0144]

In addition, before allowing the supply liquid to pass through the polyimide-based resin porous membrane, a solution such as alcohol such as methanol, ethanol, or isopropyl alcohol, a ketone such as acetone or methyl ethyl ketone, water, or a solvent contained in the supply liquid or a mixture thereof may be brought into contact with the polyimide-based resin porous membrane to be allowed to pass, for washing the polyimide-based resin porous membrane, improving the wettability with respect to the supply liquid, or adjusting the surface energy between the polyimide-based resin porous membrane and the supply liquid.

In order to bring the above solution into contact with the polyimide-based resin porous membrane, the polyimide-based resin porous membrane may be impregnated or dipped in the above solution. In a case where the above solution is brought into contact

with the polyimide-based resin porous membrane, for example, the solution can be permeated into the pores inside the polyimide-based resin porous membrane. The bringing of the solution into contact with the polyimide-based resin porous membrane may be carried out in a state where the differential pressure described above is provided, and it is preferably carried out under pressurization particularly in a case where the solution is allowed to permeate into the pores inside the polyimide-based resin porous membrane.

[0145]

<Another step>

The manufacturing method according to the present embodiment may include other steps in addition to the step (i). Examples of the other steps include a step of carrying out filtering with a filter other than the filter having a polyimide-based resin porous membrane. The filter other than the filter having a polyimide-based resin porous membrane is not particularly limited; however, examples thereof include a filter having a porous membrane of a thermoplastic resin, such as a nylon membrane, a polyethylene membrane, a polypropylene membrane, a polytetrafluoroethylene (PTFE) membrane, a tetrafluoroethylene / perfluoroalkyl vinyl ether copolymer (PFA) membrane, or a membrane obtained by modifying these membranes. Among the above, as the other filter, a filter having a porous membrane containing a polyethylene resin is preferable since it is excellent in the performance of the foreign substance removal.

[0146]

In regard to step (ii):

The manufacturing method according to the present embodiment preferably further includes a step (ii) of filtering the resist composition after the step (i) with a filter having a porous membrane containing a polyethylene resin.

A porous membrane (hereinafter, also referred to as a “polyethylene resin porous membrane”) containing a polyethylene resin may be composed of only a polyethylene resin or may contain a polyethylene resin and another resin; however, it is preferably composed of only a polyethylene resin.

5 The polyethylene resin porous membrane is not particularly limited, and a publicly known one can be used. Since the polyethylene resin porous membrane is excellent in impact resistance, abrasion resistance, and chemical resistance, it is preferable to use a porous membrane of an ultrahigh molecular weight polyethylene (UPE).

10 The average pore diameter of such a polyethylene resin porous membrane is not particularly limited; however, it is preferably in a range of 0.1 to 100 nm, more preferably in a range of 0.3 to 50 nm, and still more preferably in a range of 0.5 to 10 nm, from the viewpoint of removing fine foreign substances.

[0147]

15 Examples of such a filter having a polyethylene resin porous membrane include those in which a polyethylene resin porous membrane is provided in an outer container made of a thermoplastic resin (polyethylene, polypropylene, PFA, polyether sulfone (PES), polyimide, polyamide-imide, or the like).

[0148]

20 The step (ii) is preferably carried out after the step (i), and in this case, the average pore diameter of the polyethylene resin porous membrane is preferably smaller than the average pore diameter of the interconnection pores of the polyimide-based porous membrane.

 In the manufacturing method according to the present embodiment, the step (ii)
25 may be repeated after the step (i). In this case, the silicon-containing resin composition

(the supply liquid) is allowed to pass through a filter having a polyimide-based resin porous membrane and a filter having a polyethylene resin porous membrane, while being circulated at all times. In a case of carrying out circulation-type filtration as described above, it is preferable that both filters are arranged so that the silicon-containing resin composition passes through the filter having a polyimide-based resin porous membrane and then passes through the filter having a polyethylene resin porous membrane in the circulation path.

[0149]

In a case where the step (ii) is carried out, before allowing the supply liquid to pass through the polyethylene resin porous membrane, a solution such as alcohol such as methanol, ethanol, or isopropyl alcohol, a ketone such as acetone or methyl ethyl ketone, water, or a solvent contained in the supply liquid or a mixture thereof may be brought into contact with the polyethylene resin porous membrane to be allowed to pass in the same manner as described in the step (i), for washing the polyethylene resin porous membrane, improving the wettability with respect to the supply liquid, or adjusting the surface energy between the polyethylene resin porous membrane and the supply liquid.

[0150]

<Silicon-containing resin composition>

The silicon-containing resin composition which is a filtration target contains a silicon-containing resin (A) having a main chain consisting of a siloxane bond (hereinafter, also referred to as a “component (A)”), a siloxane bond-containing cage compound (C) other than the component (A) (hereinafter, also referred to as a “component (C)”), and an organic solvent component (S) (hereinafter, also referred to as an “component (S)”).

The silicon-containing resin composition may contain other optional

components, as necessary, in addition to the component (A), the component (C), and the component (S). The silicon-containing resin composition is, for example, a silicon-containing resin composition that is suitable as a composition for forming a resist lower layer film, which is used in a process of manufacturing a semiconductor element or the like.

[0151]

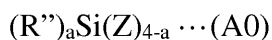
<<Silicon-containing resin (A) having main chain consisting of siloxane bond>>

The silicon-containing resin that is used in the silicon-containing resin composition according to the present embodiment has a main chain consisting of a siloxane bond (Si-O-Si bond), and it does not include those having a siloxane bond only in the side chain.

Such a component (A) may be any resin containing silicon and is preferably a polysiloxane. The polysiloxane is not particularly limited as long as it is a polymer having a siloxane bond; however, it is preferably a hydrolyzed condensate of a compound including a hydrolyzable silane compound represented by General Formula (A0).

Regarding the hydrolyzable silane compound that is used for the synthesis of polysiloxane, one kind thereof may be used alone, or two or more kinds thereof may be used in combination.

[0152]



[0153]

In General Formula (A0), R'' is a hydrogen atom, a fluorine atom, an alkyl group having 1 to 5 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, an aryl group having 6 to 20 carbon atoms, or a cyano group.

A part or all of hydrogen atoms contained in the alkyl group may be substituted with an epoxyalkyloxy group, an epoxy group, an acid anhydride group, or a cyano group.

5 A part or all of hydrogen atoms contained in the aryl group may be substituted with a hydroxy group.

Z represents a halogen atom or -OR'. R' represents a monovalent organic group.

a means the number of R'''s that are bonded to Si. 4-a means the number of Z's that are bonded to Si. a represents an integer in a range of 0 to 3. In a case where
10 there are a plurality of R'''s and a plurality of Z's, the plurality of R'''s and the plurality of Z's may be the same or different from each other.

[0154]

In General Formula (A0), examples of the alkyl group having 1 to 5 carbon atoms in R'' include a linear alkyl group such as a methyl group, an ethyl group, an n-
15 propyl group, an n-butyl group, or an n-pentyl group; and a branched alkyl group such as an isopropyl group, an isobutyl group, a sec-butyl group, a t-butyl group, or an isoamyl group. Among these, a linear alkyl group is preferable, and a methyl group is more preferable.

Examples of the alkenyl group in R'' include a group obtained by removing one
20 hydrogen atom from an alkene compound, and examples thereof include an ethenyl group, a 1-propen-1-yl group, a 1-propen-2-yl group, a 1-propen-3-yl group, a 1-buten-1-yl group, a 1-buten-2-yl group, a 1-buten-3-yl group, a 1-buten-4-yl group, a 2-buten-1-yl group, a 2-buten-2-yl group, a 1-penten-5-yl group, a 2-penten-1-yl group, a 2-penten-2-yl group, a 1-hexen-6-yl group, a 2-hexen-1-yl group, and a 2-hexen-2-yl group.

25 Examples of the aryl group in R'' include a phenyl group, a naphthyl group, a

methylphenyl group, an ethylphenyl group, a chlorophenyl group, a bromophenyl group, and a fluorophenyl group. Among these, a phenyl group or a methylphenyl group is preferable. It is noted that aryl group here includes an aralkyl group.

[0155]

- 5 The “epoxy group” in the epoxyalkyloxy group includes an oxiranyl group and an oxetanyl group, and examples of the epoxyalkyloxy group which may substitute the alkyl group include a glycidyloxy group and an oxetanylmethyloxy group.

[0156]

- Examples of the epoxy group which may be substituted with the alkyl group
10 include an oxiranyl group and an oxetanyl group.

 Examples of the acid anhydride group which may substitute the alkyl group include a succinic acid anhydride group, a maleic acid anhydride group, and a glutaric acid anhydride group.

[0157]

- 15 Examples of the alkyl group substituted with glycidyloxy group include a 2-glycidyloxyethyl group, a 3-glycidyloxypropyl group, and a 4-glycidyloxybutyl group. Among these, a 3-glycidyloxypropyl group is more preferable.

- Examples of the alkyl group substituted with the oxetanylmethyloxy group include a 3-ethyl-3-oxetanylmethyloxypropyl group, a 3-methyl-3-
20 oxetanylmethyloxypropyl group, a 3-ethyl-2-oxetanylmethyloxypropyl group, and a 2-oxetanylmethyloxyethyl group. Among these, a 3-ethyl-3-oxetanylmethyloxypropyl group is preferable.

[0158]

- Examples of the alkyl group substituted with the acid anhydride group include a
25 2-succinic acid anhydride group-substituted ethyl group, a 3-succinic acid anhydride

group-substituted propyl group, and a 4-succinic acid anhydride group-substituted butyl group. Among these, a 3-succinic acid anhydride group-substituted propyl group is more preferable.

Examples of the alkyl group substituted with the cyano group include a 2-cyanoethyl group, a 3-cyanopropyl group, and a 4-cyanobutyl group.

[0159]

Examples of the aryl group substituted with the hydroxy group include a 4-hydroxyphenyl group, a 4-hydroxy-2-methylphenyl group, and a 4-hydroxynaphthyl group. Among these, a 4-hydroxyphenyl group is more preferable.

10 [0160]

R'' is preferably an alkyl group having 1 to 5 carbon atoms or an aryl group having 6 to 20 carbon atoms.

Alternatively, R'' is preferably an aryl group having 6 to 20 carbon atoms and is more preferably a phenyl group. That is, the silicon-containing resin (A) preferably contains a phenyl group.

[0161]

In General Formula (A0), examples of the halogen atom in Z include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

[0162]

20 Examples of the monovalent organic group in R' include an alkyl group and an alkylcarbonyl group. Here, the alkyl group is preferably a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, or a t-butyl group, where a methyl group is more preferable. The alkylcarbonyl group here is preferably a methylcarbonyl group or an ethylcarbonyl group. R' is preferably an alkyl group.

25

[0163]

In General Formula (A0), a is preferably an integer in a range of 0 to 2, and more preferably 0 or 1.

[0164]

- 5 Specific examples of the hydrolyzable silane compound represented by General Formula (A0) include aromatic ring-containing trialkoxysilanes such as phenyltrimethoxysilane, 4-methylphenyltrimethoxysilane, 4-ethylphenyltrimethoxysilane, 4-hydroxyphenyltrimethoxysilane, 3-methylphenyltrimethoxysilane, 3-ethylphenyltrimethoxysilane, 3-hydroxyphenyltrimethoxysilane, 2-methylphenyltrimethoxysilane, 2-ethylphenyltrimethoxysilane, 2-hydroxyphenyltrimethoxysilane, and 2,4,6-trimethylphenyltrimethoxysilane; alkyltrialkoxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, methyltri-n-propoxysilane, methyltri-iso-propoxysilane, methyltri-n-butoxysilane, methyltri-sec-butoxysilane, methyltri-t-butoxysilane,
- 15 methyltriphenoxysilane, methyltriacetoxysilane, methyltrichlorosilane, methyltriisopropenoxysilane, methyltris(dimethylsiloxy)silane, methyltris(methoxyethoxy)silane, methyltris(methylethylketoxime)silane, methyltris(trimethylsiloxy)silane, methylsilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethyltri-n-propoxysilane, ethyltri-iso-propoxysilane, ethyltri-n-butoxysilane, ethyltri-sec-butoxysilane, ethyltri-t-butoxysilane, ethyltriphenoxysilane, ethylbistris(trimethylsiloxy)silane, ethyldichlorosilane, ethyltriacetoxysilane, ethyltrichlorosilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, n-propyltri-n-propoxysilane, n-propyltri-iso-propoxysilane, n-propyltri-n-butoxysilane, n-propyltri-sec-butoxysilane, n-propyltri-t-butoxysilane, n-propyltriphenoxysilane, n-propyltriacetoxysilane, n-propyltrichlorosilane, iso-propyltrimethoxysilane, iso-
- 20 propyltriacetoxysilane, n-propyltrichlorosilane, iso-propyltrimethoxysilane, iso-
- 25 propyltriacetoxysilane, n-propyltrichlorosilane, iso-propyltrimethoxysilane, iso-

- propyltriethoxysilane, iso-propyltri-n-propoxysilane, iso-propyltri-iso-propoxysilane, iso-propyltri-n-butoxysilane, iso-propyltri-sec-butoxysilane, iso-propyltri-t-butoxysilane, iso-propyltriphenoxysilane, n-butyltrimethoxysilane, n-butyltriethoxysilane, n-butyltri-n-propoxysilane, n-butyltri-iso-propoxysilane, n-butyltri-n-butoxysilane, n-butyltri-sec-butoxysilane, n-butyltri-t-butoxysilane, n-butyltriphenoxysilane, n-butyltrichlorosilane, 2-methylpropyltrimethoxysilane, 2-methylpropyltriethoxysilane, 2-methylpropyltri-n-propoxysilane, 2-methylpropyltri-iso-propoxysilane, 2-methylpropyltri-n-butoxysilane, 2-methylpropyltri-sec-butoxysilane, 2-methylpropyltri-t-butoxysilane, 2-methylpropyltriphenoxysilane, 1-methylpropyltrimethoxysilane, 1-methylpropyltriethoxysilane, 1-methylpropyltri-n-propoxysilane, 1-methylpropyltri-iso-propoxysilane, 1-methylpropyltri-n-butoxysilane, 1-methylpropyltri-sec-butoxysilane, 1-methylpropyltri-t-butoxysilane, 1-methylpropyltriphenoxysilane, t-butyltrimethoxysilane, t-butyltriethoxysilane, t-butyltri-n-propoxysilane, t-butyltri-iso-propoxysilane, t-butyltri-n-butoxysilane, t-butyltri-sec-butoxysilane, t-butyltri-t-butoxysilane, t-butyltriphenoxysilane, and t-butyldichlorosilane;
- alkenyltrialkoxysilanes such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri-n-propoxysilane, vinyltriisopropoxysilane, vinyltri-n-butoxysilane, vinyltri-sec-butoxysilane, vinyltri-t-butoxysilane, vinyltriphenoxysilane, allyltrimethoxysilane, allyltriethoxysilane, allyltri-n-propoxysilane, allyltriisopropoxysilane, allyltri-n-butoxysilane, allyltri-sec-butoxysilane, allyltri-t-butoxysilane, and allyltriphenoxysilane;
- tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetra-iso-propoxysilane, tetra-n-butoxysilane, tetra-sec-butoxysilane, and tetra-t-butoxysilane; tetraarylsilanes such as tetraphenoxysilanes; epoxy group-containing silanes such as oxetanyltrimethoxysilane, oxiranyltrimethoxysilane, oxiranylmethyltrimethoxysilane, and 3-glycidyloxypropyltrimethoxysilane; acid

anhydride group-containing silanes such as 3-(trimethoxysilyl)propylsuccinic acid anhydride, 2-(trimethoxysilyl)ethylsuccinic acid anhydride, 3-(trimethoxysilyl)propylmaleic acid anhydride, and 2-(trimethoxysilyl)ethylglutaric acid anhydride; and tetrahalosilanes such as tetrachlorosilane.

5 [0165]

Among these, tetramethoxysilane, phenyltrimethoxysilane, 4-methylphenyltrimethoxysilane, or methyltrimethoxysilane is preferable.

[0166]

In the synthesis of polysiloxane, in addition to the hydrolyzable silane compound represented by General Formula (A0), other silane compounds such as
10 disilanes, polycarbosilanes, and trimethoxysilanes may be used.

[0167]

As a method of hydrolyzing and condensing a compound including the hydrolyzable silane compound represented by General Formula (A0) and the other silane
15 compounds that are used as necessary, a publicly known method of hydrolysis and condensation can be used.

[0168]

In the silicon-containing resin composition according to the present embodiment, as the component (A), a resin containing silicon other than the hydrolyzed
20 condensate of the compound including the hydrolyzable silane compound represented by General Formula (A0) described above may be used alone or in combination with the hydrolyzed condensate.

Examples of the resin containing silicon other than the hydrolyzed condensate include a silsesquioxane resin.

25 [0169]

As the component (A), it is preferable to use a hydrolyzed condensate of a compound including the hydrolyzable silane compound represented by General Formula (A0), it is more preferable to use a condensate of a hydrolyzable silane compound represented by General Formula: $R''\text{-Si(OR')}_3$ from the viewpoint that the effect of the present invention is more easily obtained, and it is particularly preferable to include a condensate of the hydrolyzable silane compound in which a part or all of R'' 's are a phenyl group.

[0170]

The weight average molecular weight (M_w) (in terms of the polystyrene equivalent value determined by gel permeation chromatography (GPC)) of the component (A) is not particularly limited, and it is, for example, 200 or more, preferably in a range of 200 to 50,000, and more preferably in a range of 300 to 30,000.

In a case where the M_w of the component (A) is equal to or smaller than the upper limit value of the above-described preferred range, the solubility in an organic solvent is further improved. On the other hand, in a case where the M_w of the component (A) is equal to or larger than the lower limit value of the above-described preferred range, the adhesiveness of a resist pattern to formed to a support and the etching selectivity are likely to be enhanced.

[0171]

The content of the component (A) in the silicon-containing resin composition according to the present embodiment may be adjusted depending on the coating film thickness to be formed.

The proportion of the component (A) in the silicon-containing resin composition is preferably 0.1% by mass or more, more preferably 0.1% to 20% by mass, and still more preferably 0.5% to 15% by mass, with respect to the total mass of the silicon-

containing resin composition. In a case where the proportion is 0.5% by mass or more, the coatability on the support, the adhesiveness of the resist pattern to be formed to the support, and the etching selectivity are further enhanced.

[0172]

5 <<Siloxane bond-containing cage compound (C)>>

The siloxane bond-containing cage compound (the component (C)) in the present embodiment is a siloxane having a polyhedral structure, and it is a substance having an organic functional group at each apex.

The component (C) is not particularly limited, and it may be a so-called
10 complete cage compound or may be an incomplete cage compound.

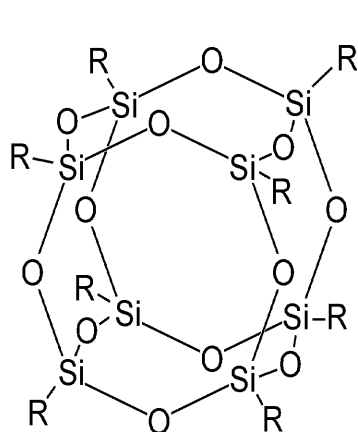
[0173]

Examples of the complete cage compound include a compound represented by General Formula (c1-1) and a compound represented by General Formula (c1-2).

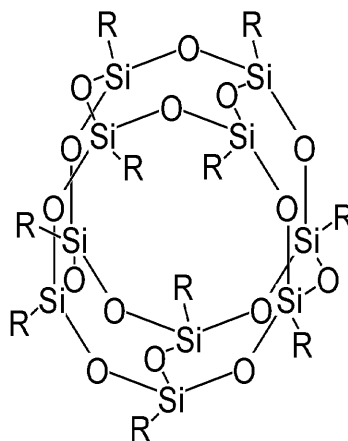
Examples of the incomplete cage compound include a compound represented by
15 General Formula (c2-1) and a compound represented by General Formula (c2-2).

[0174]

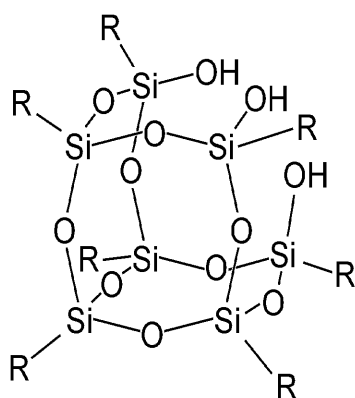
[Chemical Formula 4]



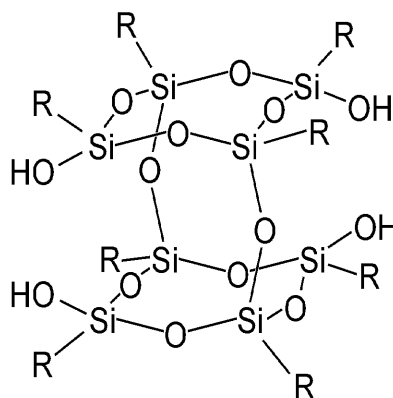
(c 1-1)



(c 1-2)



(c 2-1)



(c 2-2)

[0175]

- 5 R in the above-described general formulae is an organic group. Examples of the organic group in R include a reactive group such as a lactone-containing cyclic group, a hydrocarbon group containing an ester bond, and an epoxy group-containing group; and an alkyl group.

It is noted that it is known that the cage compound represented by the above-
 10 described general formula is generated in a trace amount in a case of manufacturing a silicon-containing compound in the related art. Depending on the difference in the

reactivity of the compound which is a monomer of the silicon-containing resin, the stability of the product generated by condensation, and the like, a complete cage compound or an incomplete cage compound is obtained.

[0176]

5 The molecular weight of the component (C) is not particularly limited, and it is, for example, 200 or more, preferably 250 to 2,000, more preferably 300 to 1,500, and still more preferably 400 to 1,000.

[0177]

10 In the silicon-containing resin composition in the present embodiment, one kind of the component (C) may be used alone, or two or more kinds thereof may be used.

From the viewpoint that defects in the coating film are relatively unlikely to occur, a complete cage compound is preferable, and a compound represented by General Formula (c1-1) or a compound represented by General Formula (c1-2) is more preferable.

15 On the other hand, from the viewpoint of usefulness of the present invention, an incomplete cage compound is preferable, and a compound represented by General Formula (c2-1) or a compound represented by General Formula (c2-2) is more preferable among the components (C).

[0178]

20 In the silicon-containing resin composition according to the present embodiment, the content of the component (C) is preferably more than 0 parts by mass and 1 part by mass or less, more preferably 0.0001 parts by mass or more and 0.5 parts by mass or less, still more preferably 0.0005 parts by mass or more and 0.5 parts by mass or less, and particularly preferably 0.001 parts by mass or more and 0.5 parts by mass or
25 less, with respect to 10 parts by mass of the component (A).

In the silicon-containing resin composition according to the present embodiment, by containing the siloxane bond-containing cage compound (the component (C)) together with the component (A), the occurrence of defects during the formation of a coating film is easily suppressed. In addition, in a case where the content of the component (C) is within the above-described preferred range, the effect of the present invention is easily obtained stably.

[0179]

<<Organic solvent component (S)>>

The silicon-containing resin composition according to the present embodiment can be manufactured by dissolving the resist materials in an organic solvent component (hereinafter, referred to as a “component (S)”).

The component (S) may be any organic solvent which can dissolve each of the components to be used to obtain a homogeneous solution, and an optional organic solvent can be appropriately selected from those which are publicly known in the related art as solvents for a chemical amplification-type resist composition and then used.

Examples of the component (S) include water; lactones such as γ -butyrolactone; ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl-n-pentyl ketone, methyl isopentyl ketone, 2-heptanone, ethylene carbonate, and propylene carbonate; polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol; polyhydric alcohol derivatives [among these, propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), and propylene glycol monoethyl ether are preferable] such as compounds having an ester bond, such as ethylene glycol monoacetate, diethylene glycol monoacetate, propylene glycol monoacetate, or dipropylene glycol monoacetate, and compounds having an ether bond, such as monoalkyl ethers (such as monomethyl ethers, monoethyl ethers,

monopropyl ethers, or monobutyl ethers of the above-described polyhydric alcohols or the above-described compounds having an ester bond) or monophenyl ethers; cyclic ethers such as dioxane; esters such as methyl lactate, ethyl lactate (EL), methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, and ethyl ethoxypropionate; aromatic organic solvents such as anisole, ethylbenzyl ether, cresylmethyl ether, diphenyl ether, dibenzyl ether, phenetole, butylphenyl ether, ethyl benzene, diethyl benzene, pentyl benzene, isopropyl benzene, toluene, xylene, cymene and mesitylene; and dimethylsulfoxide (DMSO).

In the silicon-containing resin composition in the present embodiment, the component (S) may be used alone or as a mixed solvent of two or more kinds thereof. For example, the component (S) may be a mixed solvent of water and an organic solvent. [0180]

The content of the component (S) in the silicon-containing resin composition is, for example, 70% by mass or more, and from the viewpoint of the coatability on the support, it may be 80% by mass or more or may be 90% by mass or more, with respect to the total mass (100% by mass) of the silicon-containing resin composition. [0181]

<<Other components>>

The silicon-containing resin composition which is a filtration target may further contain other components in addition to the component (A), the component (C), and the component (S), which are described above. Publicly known components blended into a composition for forming a silicon-containing lower layer film, which is formed by using a silicon-containing resin as a base material component in the related art, can be used as the other components. Examples of such other components include a photoacid generator, a crosslinking agent, a thermal crosslinking accelerator, an organic acid, an

ether compound, and a surfactant.

[0182]

In regard to the photoacid generator:

The silicon-containing resin composition may further contain a photoacid
5 generator that generates an acid upon exposure. Examples of such a photoacid
generator are numerous and include onium salt-based acid generators such as iodonium
salts and sulfonium salts; oxime sulfonate-based acid generators; diazomethane-based
acid generators such as bisalkyl or bisaryl sulfonyl diazomethanes and poly(bis-
sulfonyl)diazomethanes; nitrobenzyl sulfonate-based acid generators; iminosulfonate-
10 based acid generators; and disulfone-based acid generators. Specific examples of the
photoacid generator include the materials disclosed in paragraphs 0160 to 0179 of
Japanese Unexamined Patent Application, First Publication No. 2009-126940.

[0183]

In regard to crosslinking agent:

15 The silicon-containing resin composition may further contain a crosslinking
agent. Examples of the crosslinking agent include a melamine-based crosslinking
agent, a urea-based crosslinking agent, an alkylene urea-based crosslinking agent, a
glycoluril-based crosslinking agent, a phenol-based crosslinking agent, and an epoxy-
based crosslinking agent.

20 It is noted that the term “lower” used below means having 1 to 5 carbon atoms.

[0184]

Examples of the melamine-based crosslinking agent include a compound
obtained by reacting melamine with formaldehyde to substitute a hydrogen atom of an
amino group with a hydroxymethyl group; and a compound obtained by reacting
25 melamine, formaldehyde, and a lower alcohol to substitute a hydrogen atom of an amino

group with a lower alkoxymethyl group. Specific examples thereof include hexamethoxymethyl melamine, hexaethoxymethyl melamine, hexapropoxymethyl melamine, and hexabutoxybutyl melamine, among which hexamethoxymethyl melamine is preferable.

5 [0185]

Examples of the urea-based crosslinking agent include a compound obtained by reacting urea with formaldehyde to substitute a hydrogen atom of an amino group with a hydroxymethyl group; and a compound obtained by reacting urea, formaldehyde, and a lower alcohol to substitute a hydrogen atom of an amino group with a lower

10 alkoxymethyl group. Specific examples thereof include bismethoxymethyl urea, bisethoxymethyl urea, bispropoxymethyl urea, and bisbutoxymethyl urea, among which bismethoxymethyl urea is preferable.

[0186]

The alkylene urea-based crosslinking agent can be obtained by subjecting an

15 alkylene urea to a condensation reaction with formalin or by subjecting the product of this reaction to a reaction with a lower alcohol.

Specific examples of the alkylene urea-based crosslinking agent include ethylene urea-based crosslinking agents such as mono- and/or dihydroxymethylated ethylene urea, mono- and/or dimethoxymethylated ethylene urea, mono- and/or

20 diethoxymethylated ethylene urea, mono- and/or dipropoxymethylated ethylene urea, and mono- and/or dibutoxymethylated ethylene urea; propylene urea-based crosslinking agents such as mono- and/or dihydroxymethylated propylene urea, mono- and/or dimethoxymethylated propylene urea, mono- and/or diethoxymethylated propylene urea, mono- and/or dipropoxymethylated propylene urea, and mono- and/or

25 dibutoxymethylated propylene urea; 1,3-di(methoxymethyl) 4,5-dihydroxy-2-

imidazolidinone; and 1,3-di(methoxymethyl)-4,5-dimethoxy-2-imidazolidinone.

[0187]

Examples of the glycoluril-based crosslinking agent include a glycoluril derivative having a substitution with one or both of a hydroxyalkyl group and an alkoxyalkyl group having 1 to 4 carbon atoms at the N-position. Such a glycoluril derivative can be obtained by subjecting glycoluril to a condensation reaction with formalin or by subjecting the product of this reaction to a reaction with a lower alcohol.

Specific examples of the glycoluril-based crosslinking agents include mono-, di-, tri-, and/or tetra-hydroxymethylated glycoluril; mono-, di-, tri-, and/or tetra-methoxymethylated glycoluril; mono-, di-, tri-, and/or tetra-ethoxymethylated glycoluril; mono-, di-, tri-, and/or tetra-propoxymethylated glycoluril; and mono-, di-, tri-, and/or tetra-butoxymethylated glycoluril.

[0188]

The phenol-based crosslinking agent is not particularly limited as long as it is a compound having a plurality of phenolic core structures in the same molecule, and any phenol-based crosslinking agent can be selected and used. In a case where a plurality of phenolic core structures is contained, crosslinking reactivity is improved.

The number of phenolic core structures is preferably 2 to 5, more preferably 2 to 4, and still more preferably 2 or 3.

[0189]

The epoxy-based crosslinking agent is not particularly limited as long as it has an epoxy group, and any epoxy-based crosslinking agent can be selected and used.

Among the above, the one having two or more epoxy groups is preferable. In a case where two or more epoxy groups are contained, crosslinking reactivity is improved.

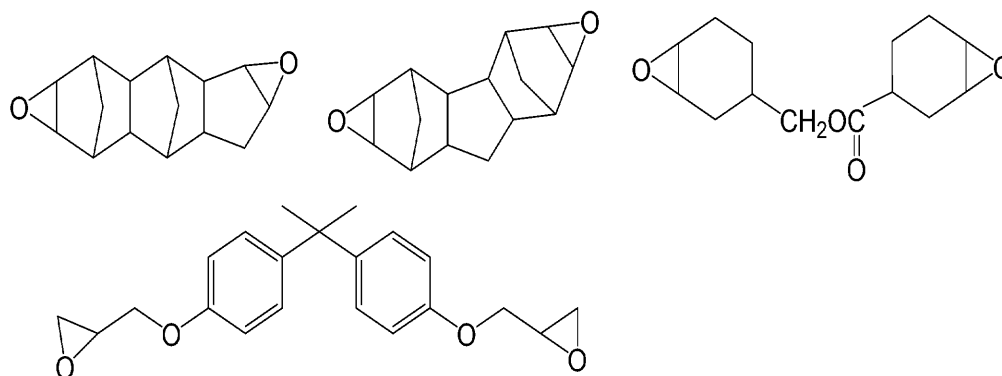
The number of epoxy groups is preferably 2 or more, more preferably 2 to 4, and

most preferably 2.

Suitable epoxy-based crosslinking agents are shown below.

[0190]

[Chemical Formula 5]



5

[0191]

In regard to thermal crosslinking accelerator:

The silicon-containing resin composition may further contain a thermal crosslinking accelerator. Specific examples of the thermal crosslinking accelerator include the materials disclosed in Japanese Unexamined Patent Application, First Publication No. 2007-302873.

10

[0192]

In regard to organic acid:

In order to improve the stability of the composition, the silicon-containing resin composition may further contain an organic acid. Examples of such an organic acid include an organic acids having 1 to 30 carbon atoms, which is monovalent or divalent or higher valent, and examples thereof include formic acid, acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, oleic acid, stearic acid, linoleic acid, linolenic acid, benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, salicylic acid, trifluoroacetic acid,

20

monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, oxalic acid, malonic acid, methylmalonic acid, ethylmalonic acid, propylmalonic acid, butylmalonic acid, dimethylmalonic acid, diethylmalonic acid, succinic acid, methylsuccinic acid, glutaric acid, adipic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, and citric acid.

- 5 Among these, oxalic acid, maleic acid, formic acid, acetic acid, propionic acid, citric acid, or the like is preferable. One kind of organic acid may be used alone, or two or more kinds thereof may be used in combination.

[0193]

In regard to ether compound:

- 10 The silicon-containing resin composition may further contain an ether compound as a stabilizer for the composition. Examples of such an ether compound include an alcohol having a cyclic ether as a substituent, which is monovalent or divalent or higher valent, and specific examples thereof include the materials disclosed in paragraphs 0181 to 0184 of Japanese Unexamined Patent Application, First Publication
- 15 No. 2009-126940. Among these, suitable examples thereof include a crown ether derivative and a compound having, as a substituent, a bicyclo ring in which an oxygen atom is at the bridgehead position.

[0194]

In regard to surfactant:

- 20 The silicon-containing resin composition may contain a surfactant as necessary. Such a surfactant is preferably a nonionic surfactant, and examples thereof include a perfluoroalkyl polyoxyethylene ethanol, a fluorinated alkyl ester, a perfluoroalkylamine oxide, a perfluoroalkyl ethylene oxide adduct, and a fluorine-containing organosiloxane-based compound. Specific examples thereof include the materials disclosed in
- 25 paragraph 0185 of Japanese Unexamined Patent Application, First Publication No. 2009-

126940.

[0195]

As desired, miscible additives such as an additive resin, a dissolution inhibitor, a plasticizer, a stabilizer, a coloring agent, a halation prevention agent, and a dye for

5 improving the performance of the coating film can be added as appropriate to the silicon-containing resin composition which is a filtration target.

[0196]

In the silicon-containing resin composition purified product manufacturing method according to the present aspect described above, a filtration target (a silicon-

10 containing resin composition) is filtered in the above-described step (i) by using a filter having a porous membrane (polyimide porous membrane or the like) that has a porous structure in which adjacent spherical cells are connected to each other and contains at least one kind of resin skeleton selected from the group consisting of polyimide and polyamide-imide. As a result, foreign substances such as an organic substance and a
15 metal impurity are removed from the filtration target more than ever. The reason why such an effect of removing foreign substances is obtained is not clear; however, it is considered that the effect of removing foreign substances is obtained by combining the effect of a filter equipped with a polyimide porous membrane or the like, where the filter has two effects of impurity removal functions, that is, the adsorption effect and the
20 sieving effect, and the effect of increasing the contact probability between the surface of the filter and the impurities due to the filter structure.

Therefore, according to the manufacturing method according to the present aspect, it is possible to manufacture a silicon-containing resin composition purified product in which impurities are further reduced and the occurrence of defects during the
25 formation of a coating film is suppressed.

[0197]

The filter in the present aspect is not limited to the one that includes a porous membrane in which the interconnection pores 5 in which the adjacent spherical cell 1a and the spherical cell 1b are connected to each other as shown in FIG. 1 is formed, and
5 may include a porous membrane in which, in addition to the interconnection pores 5 in which the spherical cells 1a and 1b are connected to each other, a cell or interconnection pore having another form is formed.

Examples of the cell (hereinafter, referred to as "another cell") having another form include a cell that differs in shape or pore diameter, and examples thereof include
10 an elliptical cell, a polyhedral cell, and a spherical cell having a different pore diameter. Examples of the above-described "interconnection pore having another form" include an interconnection pore in which a spherical cell and another cell are connected to each other.

The shape or pore diameter of another cell may be appropriately determined
15 depending on the kinds of impurities to be removed. The interconnection pore in which a spherical cell and another cell are connected to each other can be formed, for example, by selecting a material of the fine particle described above or controlling the shape of the fine particles.

According to the filter including a porous membrane in which, in addition to the
20 interconnection pore in which adjacent spherical cells are connected to each other, a cell or interconnection pore having another form is formed, it is possible to efficiently remove various foreign substances from a filtration target.

[0198]

In addition, the filter having a polyimide-based resin porous membrane, which is
25 used in the filtration step, replace a filter cartridge or the like for removing impurities

having a fine particle shape, which has been installed in the related art, in the supply line of the silicon-containing resin composition or the point of use (POU) in the semiconductor manufacturing process or can be used in combination with these. As a result, various foreign substances can be efficiently removed from a filtration target using the same device and operation as those in the related art, and a silicon-containing resin composition purified product having high purity can be manufactured.

[0199]

(Pattern formation method)

A pattern formation method according to a second aspect of the present invention includes the following step (x) and step (y).

Step (x): a step of obtaining a silicon-containing resin composition purified product by the silicon-containing resin composition purified product manufacturing method according to the first aspect

Step (y): a step of forming a silicon-containing resist lower layer film on a support using the silicon-containing resin composition purified product, forming an upper layer resist film on the silicon-containing resist lower layer film using an upper layer resist film composition, forming an upper layer resist pattern on the upper layer resist film, transferring a pattern to the silicon-containing resist lower layer film by etching using the upper layer resist pattern as a mask, and transferring a pattern to the support by etching using, as a mask, the silicon-containing resist lower layer film having the transferred pattern

The pattern formation method according to the present aspect can be carried out, for example, as follows.

[0200]

In the step (x), <Step (i)> described above is carried out to obtain a silicon-

containing resin composition purified product.

[0201]

In regard to step (y):

As the support, the following support can be used: a semiconductor substrate; a
 5 support on which any of a metal film, a metal carbide film, a metal oxide film, a metal
 nitride film, a metal oxycarbide film, or a metal oxynitride film is formed on a
 semiconductor substrate as a layer to be processed; or the like.

[0202]

As the semiconductor substrate, a silicon substrate is generally used; however, it
 10 is not particularly limited. Si, amorphous silicon (α -Si), p-Si, SiO₂, SiN, SiON, W, TiN,
 Al, or the like may be used.

In addition, as the metal constituting the support, any one of silicon, titanium,
 tungsten, hafnium, zirconium, chromium, germanium, copper, aluminum, indium,
 gallium, arsenic, palladium, iron, tantalum, iridium, or molybdenum, or an alloy thereof
 15 can be used. As a layer to be processed, which contains such a metal, for example, Si,
 SiO₂, SiN, SiON, SiOC, p-Si, α -Si, TiN, WSi, BPSG, SOG, Cr, CrO, CrON, MoSi, W,
 W-Si, Al, Cu, Al-Si, and various low dielectric films, as well as an etching stopper film
 thereof, are used, and the layer to be processed can be formed to have a thickness of
 usually 50 to 10,000 nm, particularly 100 to 5,000 nm.

20 [0203]

In the pattern formation method according to the present aspect, an organic
 lower layer film or an organic hard mask can be formed on the support. Among these,
 the organic lower layer film can be formed using a material for forming an organic lower
 layer film. The organic hard mask can be formed by using a CVD method from a
 25 material for forming an organic hard mask, which contains carbon as a main component.

Such an organic lower layer film and such an organic hard mask are not particularly limited; however, in a case where the pattern formation is carried out by exposure, the upper layer resist film is preferably a film that exhibits sufficient function as the antireflection film.

5 [0204]

In the pattern formation method according to the present aspect, the silicon-containing resist lower layer film can be produced on a support by a spin coating method or the like from the silicon-containing resin composition purified product.

10 In a case of forming the silicon-containing resist lower layer film by a spin coating method, for the purpose of evaporating the solvent after the spin coating and preventing mixing with the upper layer resist film, it is preferable to carry out baking in order to accelerate the crosslinking reaction. The baking temperature is preferably within a range of 50°C to 500°C, and the baking time is preferably within a range of 10 to 300 seconds.

15 [0205]

In addition, in the pattern formation method according to the present aspect, as a method of forming a pattern on the upper layer resist film, any one of the following method can be suitably used: a lithography method using light having a wavelength of 300 nm or less or EUV light; an electron beam direct drawing method; a directed self assembly method (DSA method); or a nanoimprinting lithography method.

[0206]

20 The upper layer resist film composition can be appropriately selected according to the method of forming a pattern on the upper layer resist film. For example, in a case where lithography using light of 300 nm or less or EUV light is carried out, a chemical amplification-type photoresist film material can be used as the upper layer resist film

25

composition. Examples of such a photoresist film material include a material that forms a positive-tone pattern by forming a photoresist film, carrying out exposure, and then dissolving and removing an exposed portion using an alkali developing solution, and a material that forms a negative-tone pattern by dissolving and removing an unexposed portion using a developing solution containing an organic solvent.

[0207]

According to the above-described pattern formation method according to the present aspect, since the silicon-containing resin composition purified product obtained by the silicon-containing resin composition purified product manufacturing method according to the first aspect is used, the number of defects during the formation of the coating film on the support is reduced, and thus the occurrence of defects in pattern transfer can be suppressed. As a result, an object to be processed can be processed without defects and with high accuracy, and the yield can be improved.

[0208]

In addition, according to the above-described pattern formation method according to the present aspect, since the silicon-containing resin composition purified product obtained by the silicon-containing resin composition purified product manufacturing method according to the first aspect is used, it is possible to form, in the step (y), a silicon-containing resist lower layer film having few coating defects and having excellent pattern adhesiveness and etching selectivity.

[0209]

(Silicon-containing resin composition purified product)

A silicon-containing resin composition purified product according to a third aspect of the present invention contains a silicon-containing resin (A) having a main chain consisting of a siloxane bond, a siloxane bond-containing cage compound (C) other

than the silicon-containing resin (A), and an organic solvent component (S).

The silicon-containing resin composition purified product is characterized in that the number of counting target objects having a size of 0.135 μm or more, which are counted by a light scattering-type liquid-borne particle counter, is less than 0.2

5 objects/mL.

As the light scattering-type liquid-borne particle counter, for example, KS-41 manufactured by RION Co., Ltd. can be used.

[0210]

The silicon-containing resin composition purified product according to the present aspect can be obtained by the silicon-containing resin composition purified product manufacturing method according to the first aspect described above. The silicon-containing resin composition purified product obtained by the manufacturing method according to the first aspect is a composition subjected to filtration through a filter having a polyimide-based resin porous membrane to remove foreign substances.

15 As a result, in the silicon-containing resin composition purified product according to the present aspect, the number of counting target objects having a size of 0.135 μm or more, which are counted by a light scattering-type liquid-borne particle counter, is less than 0.2 objects/mL, and thus it is possible to realize a silicon-containing resin composition purified product having a very small number of foreign substances.

20 In the silicon-containing resin composition purified product according to the present aspect, the number of counting target objects having a size of 0.135 μm or more, which are counted by a light scattering-type liquid-borne particle counter, is preferably 0.15 objects/mL or less, and more preferably 0.1 objects/mL or less.

Since the number of foreign substances is, as described above, extremely small in the silicon-containing resin composition purified product according to the present

25

aspect, the occurrence of defects during the formation of a coating film is suppressed.

Such a silicon-containing resin composition purified product makes it possible to form, in the pattern formation, a silicon-containing resist lower layer film having few coating defects and having excellent pattern adhesiveness and etching selectivity, and thus it is useful as a material for forming a lower layer film.

[0211]

In the silicon-containing resin composition purified product according to the present aspect, the content of the metal component is preferably less than 1.1 ppb, more preferably 1 ppb or less, still more preferably 0.9 ppb or less, and even still more preferably 0.85 ppb or less, where the metal component is selected from the group consisting of Li, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Sn, Ba, W, Au, and Pb.

[0212]

The silicon-containing resin composition purified product according to the present aspect can be obtained by the silicon-containing resin composition purified product manufacturing method according to the first aspect described above. The silicon-containing resin composition purified product obtained by the manufacturing method according to the first aspect is a composition subjected to filtration through a filter having a polyimide-based resin porous membrane to remove metal impurities. As a result, in the silicon-containing resin composition purified product according to the present aspect, the content of the metal component is less than 1.1 ppb, where the metal component is selected from the group consisting of Li, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Sn, Ba, W, Au, and Pb, and thus it is possible to realize a silicon-containing resin composition purified product having a very small number of metal impurities.

[0213]

The various components blended in the silicon-containing resin composition include a metal component, such as a trace amount of metal ion impurities. This metal component may be originally contained in the blending component; however, it may also
5 be mixed from a chemical liquid transfer path such as a pipe or a joint of a manufacturing device. In the silicon-containing resin composition purified product manufacturing method according to the first aspect, these metal components can be effectively removed.

In the silicon-containing resin composition purified product according to the present aspect, the content of the metal component is preferably 1 ppb or less, more
10 preferably 0.9 ppb or less, and still more preferably 0.85 ppb or less.

Since the content of the metal component is, as described above, extremely small in the silicon-containing resin composition purified product according to the present aspect, the occurrence of defects during the formation of a coating film is suppressed.

15 [0214]

The content of the metal component is the total content of Li, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Sn, Ba, W, Au, and Pb. The content of the metal component in the silicon-containing resin composition purified product can be measured using an inductively coupled plasma - mass spectrometer (ICP-MS 8900,
20 manufactured by Agilent Technologies, Inc.).

[0215]

In the preferred aspect, in the silicon-containing resin composition purified product, the number of counting target objects having a size of 0.135 μm or more, which are counted by a light scattering-type liquid-borne particle counter, is less than 0.2
25 objects/mL, and the content of the metal component is less than 1.1 ppb, where the metal

component is selected from the group consisting of Li, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Sn, Ba, W, Au, and Pb.

[0216]

It is preferable that the silicon-containing resin composition purified product
5 according to the third aspect has the same composition as the silicon-containing resin composition that is used in the silicon-containing resin composition purified product manufacturing method according to the first aspect.

[0217]

The silicon-containing resin composition purified product according to the third
10 aspect can be manufactured, for example, by a manufacturing method including the following steps (a) to (c).

Step (a): a step of filtering a resin solution prepared by dissolving the silicon-containing resin (the component (A)) in an organic solvent component (S) with a filter having a polyimide-based resin porous membrane to obtain a silicon-containing resin
15 solution purified product

Step (b): a step of mixing the silicon-containing resin solution purified product with the above-described other components to obtain a silicon-containing resin composition

Step (c): a step of filtering the silicon-containing resin composition with a filter
20 having a polyimide-based resin porous membrane

[0218]

(Pattern formation method)

A pattern formation method according to a fourth aspect of the present invention is a pattern formation method including forming a silicon-containing resist lower layer
25 film on a support using the silicon-containing resin composition purified product

according to the third aspect; forming an upper layer resist film on the silicon-containing resist lower layer film using an upper layer resist film composition; forming an upper layer resist pattern on the upper layer resist film and transferring a pattern to the silicon-containing resist lower layer film by etching using the upper layer resist pattern as a mask; and transferring a pattern to the support by etching using, as a mask, the silicon-containing resist lower layer film having the transferred pattern.

The pattern formation method according to the present aspect can be carried out in the same manner as the pattern formation method according to the second aspect described above. According to the pattern formation method according to the present aspect, since the silicon-containing resin composition purified product according to the third aspect is used, it is possible to form a silicon-containing resist lower layer film having few coating defects and having excellent pattern adhesiveness and etching selectivity.

Examples

[0219]

Hereinafter, the present invention will be described in more detail based on Examples; however, the present invention is not limited to these Examples.

[0220]

<Manufacturing of silicon-containing resin composition purified product>

(Examples 1 and 2 and Comparative Examples 1 to 4)

Each of the components shown in Table 1 was mixed and homogenized to prepare each of silicon-containing resin compositions (1) to (3) which are filtration targets.

Next, the silicon-containing resin compositions (1) to (3) were filtered through each filter to obtain a silicon-containing resin composition purified product. In any of

the examples, the filtration conditions were such that the filtration pressure was set to 0.01 MPa and the filtration temperature was set to 23°C.

[0221]

[Table 1]

Silicon-containing resin composition	Silicon-containing resin(A)	Siloxane bond-containing cage compound (C)	Organic solvent component (S)
(1)	(A)-1 [2]	(C)-1 [0.001]	(S)-1 [98]
(2)	(A)-1 [2]	(C)-1 [0.100]	(S)-1 [98]
(3)	(A)-1 [2]	-	(S)-1 [98]

5 [0222]

In Table 1, each abbreviation has the following meaning. The numerical value in the brackets indicates the blending amount (parts by mass; in terms of solid content) of each component.

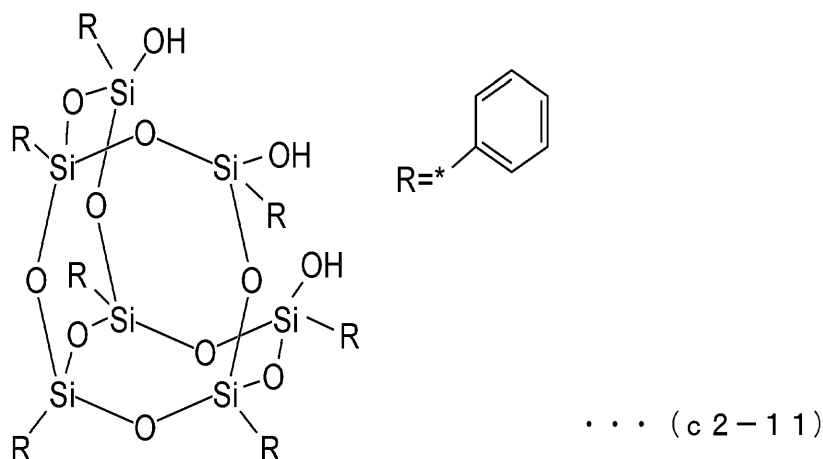
(A)-1: A condensate of R''-Si(OR')₃, that is, a condensate of
 10 phenyltrimethoxysilane (R'' = Phenyl, R' = Me) and tetramethoxysilane (R'' = MeO, R' = Me)

(C)-1: A siloxane bond-containing cage compound, which is represented by
 Chemical Formula (c2-11)

(S)-1: A mixed solvent of propylene glycol monoethyl ether/water = 90/10
 15 (mass ratio)

[0223]

[Chemical Formula 6]



[0224]

5 <<Used filter>>

Table 2 shows the filter that is used for manufacturing the silicon-containing resin composition purified product of each example.

The porous membranes in the filter (F-01) were prepared by the production method described in Japanese Unexamined Patent Application, First Publication No.

10 2017-68262.

It is noted that, for the filter (F-01), the average pore diameter of the interconnection pores in the porous membrane was measured using a Perm Porometer (manufactured by Porous Materials Inc.) according to the half-dry method (ASTM E1294-89) using perfluoropolyester (product name: Galwick, interfacial tension value:

15 15.9 dyne/cm) as the test liquid at a measurement temperature of 25°C and a measurement pressure range of 0 to 400 psi, and the results are shown in Table 2.

[0225]

[Table 2]

Filter	
(F-01)	A 10-inch filter which has a polyimide resin structure and includes a porous membrane having a porous structure in which interconnection pores obtained by connecting adjacent spherical cells to each other are formed. Average spherical cell diameter of spherical cells: 80 nm Average pore diameter of interconnection pores in porous membrane: 20 nm Size of removed particles: sub 1 nm
(F-10)	A 10-inch filter which includes a porous membrane made of an ultrahigh molecular weight polyethylene (UPE). Size of removed particles: sub 1 nm, Entegris Micro UC Filter

[0226]

(Example 1)

- 5 The silicon-containing resin composition (1) which is a filtration target was filtered through the filter (F-01) to obtain a silicon-containing resin composition purified product.

[0227]

(Example 2)

- 10 The silicon-containing resin composition (2) which is a filtration target was filtered through the filter (F-01) to obtain a silicon-containing resin composition purified product.

[0228]

(Comparative Example 1)

- 15 The silicon-containing resin composition (3) which is a filtration target was filtered through the filter (F-01) to obtain a silicon-containing resin composition purified

product.

[0229]

(Comparative Example 2)

The silicon-containing resin composition (1) which is a filtration target was
5 filtered through the filter (F-10) to obtain a silicon-containing resin composition purified product.

[0230]

(Comparative Example 3)

The silicon-containing resin composition (2) which is a filtration target was
10 filtered through the filter (F-10) to obtain a silicon-containing resin composition purified product.

[0231]

(Comparative Example 4)

The silicon-containing resin composition (3) which is a filtration target was
15 filtered through the filter (F-10) to obtain a silicon-containing resin composition purified product.

[0232]

[Evaluation of particle quantity]

In the silicon-containing resin composition purified product manufactured in
20 each example, the number of counting target objects with a size of 0.135 μm or greater was counted by a dynamic light scattering method using a light scattering-type liquid-borne particle counter [manufactured by RION Co., Ltd., model number: KS-41, light source: semiconductor laser-excited solid-state laser (wavelength: 830 nm, rated output: 0.2 W), flow amount: 10 mL/min]. The counting was carried out three times, and the
25 average value thereof was used as the counted value.

It is noted that the light scattering-type liquid-borne particle counter was used after calibration with a polystyrene latex (PSL) standard particle solution. The results are shown as “Particle quantity (particles/mL)” in Table 3.

[0233]

5 [Evaluation of coating defect]

Each of the silicon-containing resin composition purified products manufactured in each of the examples was applied onto a silicon wafer by spin coating at 1,500 rpm using a spinner, and a heating treatment was carried out on a hot plate at a temperature of 240°C for 60 seconds to produce a coating film having a film thickness of 35 nm.

10 For the surface defects (coating defects) of the coating film, the number of coating defects having a size of 50 nm or more was measured using Surfscan SP5, an unpatterned wafer defect inspection device, manufactured by KLA-Tencor Corporation. These results are shown in Table 3 as “Coating defect (defects/679 cm²)”.

[0234]

15 [Table 3]

	Filtration target	Filter	Particle quantity (particles/mL)	Coating defect (defects/679 cm ²)
	Silicon-containing resin composition			
Example 1	(1)	(F-01)	0.1	687
Example 2	(2)	(F-01)	0.1	455
Comparative Example 1	(3)	(F-01)	0.2	1516
Comparative Example 2	(1)	(F-10)	0.5	1054
Comparative Example 3	(2)	(F-10)	0.5	980
Comparative Example 4	(3)	(F-10)	0.5	5625

[0235]

From the results shown in Table 3, it has been confirmed that in the silicon-

containing resin composition purified products obtained in Examples, both the particle quantity and the coating defects (the number of defects) are reduced as compared with the silicon-containing resin composition purified products obtained in Comparative Examples.

5 [0236]

From the comparison between Example 1 and Example 2, the results are such that in the silicon-containing resin composition purified product obtained in Example 2, the coating defects (the number of defects) are reduced as compared with the silicon-containing resin composition purified product obtained in Example 1.

10 [0237]

While the preferred examples of the present invention have been described and illustrated above, it should be understood that these are exemplary of the present invention and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can be made without departing from the scope of the present invention. The present invention is not limited by the description above, but is limited only by the appended claims.

REFERENCE SIGNS LIST

[0238]

- 1a Spherical cell
- 20 1b Spherical cell
- 5 Interconnection pore

CLAIMS

[Claim 1] A silicon-containing resin composition purified product manufacturing method comprising:

- 5 a step of filtering a silicon-containing resin composition with a filter having a porous structure in which adjacent spherical cells are connected to each other, wherein the filter has a porous membrane containing at least one kind of resin selected from the group consisting of polyimide and polyamide-imide, and the silicon-containing resin composition contains
- 10 a silicon-containing resin (A) having a main chain consisting of a siloxane bond, a siloxane bond-containing cage compound (C) other than the silicon-containing resin (A), and
- an organic solvent component (S).

[Claim 2] The silicon-containing resin composition purified product manufacturing method according to Claim 1, wherein the silicon-containing resin (A) contains a phenyl

15 group.

[Claim 3] The silicon-containing resin composition purified product manufacturing method according to Claim 1 or 2, wherein an average pore diameter of the porous membrane is 10 to 1,000 nm.

[Claim 4] The silicon-containing resin composition purified product manufacturing

20 method according to Claim 1 or 2, wherein an average spherical cell diameter of the spherical cells is 20 to 2,500 nm.

[Claim 5] The silicon-containing resin composition purified product manufacturing method according to Claim 1 or 2, wherein the filter has a polyimide porous membrane.

[Claim 6] A pattern formation method comprising:

25 a step of obtaining a silicon-containing resin composition purified product by the

silicon-containing resin composition purified product manufacturing method according to Claim 1 or 2; and

5 a step of forming a silicon-containing resist lower layer film on a support using the silicon-containing resin composition purified product, forming an upper layer resist film on the silicon-containing resist lower layer film using an upper layer resist film composition, forming an upper layer resist pattern on the upper layer resist film, transferring a pattern to the silicon-containing resist lower layer film by etching using the upper layer resist pattern as a mask, and transferring a pattern to the support by etching using, as a mask, the silicon-containing resist lower layer film having the transferred
10 pattern.

[Claim 7] A silicon-containing resin composition purified product comprising:

a silicon-containing resin (A) having a main chain consisting of a siloxane bond;
a siloxane bond-containing cage compound (C) other than the silicon-containing resin (A); and
15 an organic solvent component (S),
wherein the number of counting target objects having a size of 0.135 μm or more is less than 0.2 objects/mL, where the counting target objects are counted by a light scattering-type liquid-borne particle counter.

[Claim 8] A pattern formation method comprising:

20 forming a silicon-containing resist lower layer film on a support using the silicon-containing resin composition purified product according to Claim 7;
forming an upper layer resist film on the silicon-containing resist lower layer film using an upper layer resist film composition;
forming an upper layer resist pattern on the upper layer resist film and
25 transferring a pattern to the silicon-containing resist lower layer film by etching using the

upper layer resist pattern as a mask; and

transferring a pattern to the support by etching using, as a mask, the silicon-containing resist lower layer film having the transferred pattern.