

DESCRIPTION

TITLE OF INVENTION: METHOD FOR PRODUCING PURIFIED RESIST
COMPOSITION, METHOD FOR FORMING RESIST PATTERN, AND PURIFIED
RESIST COMPOSITION

5

TECHNICAL FIELD

[0001]

The present invention relates to a method for producing a purified resist
composition, a method for forming a resist pattern, and a purified resist composition.

10

Priority is claimed on Japanese Patent Application No. 2023-027479, filed
February 24, 2024, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002]

In recent years, in the manufacture of semiconductor elements and liquid crystal
15 display elements, advances in lithography technologies have led to a rapid progress in the
field of pattern fining. Typically, these pattern fining technologies involve shortening
the wavelength (increasing the energy) of the exposure light source.

[0003]

A resist material is required to have lithography characteristics such as
20 resolution that enables reproduction of a fine-sized pattern, and sensitivity to these types
of exposure light sources. As a resist material that satisfies these requirements, a
chemically amplified resist composition that contains a base material component whose
solubility in a developing solution is changed by an action of an acid, and an acid
generator component that generates an acid upon light exposure has been used in the
25 related art.

[0004]

Recently, as a resist material suitable for reproducing a finer pattern, a resist composition containing a compound containing a metal atom as a base material component has been proposed. In a resist composition containing a metal compound as
5 a base material component, the metal compound exhibits reduced solubility in a developing solution upon exposure, and a negative-tone pattern is formed. Unlike the chemical amplification-type resist composition, this resist composition is more suitable for forming a fine pattern since acid diffusion is not involved.

[0005]

10 For example, Patent Document 1 describes a resist composition containing a complex in which an organic ligand is coordinated to a core of a metal oxide.

Citation List

Patent Document

[0006]

15 Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2021-102604

SUMMARY OF INVENTION

Technical Problem

[0007]

20 In a resist composition containing a metal compound as a base material component, a gel is generated due to agglomeration of metal cations, which causes defects during formation of a resist film. In order to form a resist pattern in which defects are reduced, it is required to suppress defects during the formation of the resist film.

25 [0008]

The present invention has been made in consideration of the above-described circumstances, and an object thereof is to provide a method for producing a purified resist composition in which impurities are further reduced and occurrence of defects during formation of a resist film can be reduced, a purified resist composition produced
5 by the production method, and a method for forming a resist pattern using the purified resist composition.

Solution to Problem

[0009]

In order to solve the above-described problems, the present invention has
10 adopted the following configurations.

[0010]

According to a first aspect of the present invention, there is provided a method for producing a purified resist composition, including: a step of filtering a resist composition through a filter having a porous structure in which adjacent spherical cells
15 communicate with each other, in which the filter includes a porous membrane containing at least one resin selected from the group consisting of polyimide and polyamide-imide, the resist composition contains a metal compound (M) and an organic solvent component (S), the metal compound (M) contains a metal ion of a metal atom in Group 3 to Group
16 in a long periodic table or a metal oxide of the metal atom, and a bonder that is
20 bonded to the metal ion or the metal oxide, and a content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to a total mass of the resist composition.

[0011]

According to a second aspect of the present invention, there is provided a
25 method for forming a resist pattern, including: a step of obtaining a purified resist

composition using the method for producing a purified resist composition according to the first aspect; a step of forming a resist film on a support using the purified resist composition; a step of exposing the resist film to light; and a step of developing the resist film exposed to light to form a resist pattern.

5 [0012]

According to a third aspect of the present invention, there is provided a purified resist composition including: a metal compound (M); and an organic solvent component (S), in which the metal compound (M) includes a metal ion of a metal atom in Group 3 to Group 16 in a long periodic table or a metal oxide of the metal atom, and a bonder that is
10 bonded to the metal ion or the metal oxide, a content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to a total mass of the purified resist composition, and the purified resist composition is formed such that the number of counting objects with a size of 0.135 μm or greater, which is counted by a light scattering type liquid-borne particle counter, is less than 1 particle/mL.

15 [0013]

According to a fourth aspect of the present invention, there is provided a method for forming a resist pattern, including: a step of forming a resist film on a support using the purified resist composition according to the third aspect; a step of exposing the resist film; and a step of developing the resist film exposed to light to form a resist pattern.

20 Advantageous Effects of Invention

[0014]

According to the present invention, it is possible to provide a method for producing a purified resist composition in which impurities are further reduced and occurrence of defects during formation of a resist film can be reduced, a purified resist
25 composition produced by the production method, and a method for forming a resist

pattern using the purified resist composition.

BRIEF DESCRIPTION OF DRAWINGS

[0015]

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

DESCRIPTION OF EMBODIMENTS

[0016]

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
10 compound, or the like that has no aromaticity.

The term “alkyl group” includes a linear, branched, or cyclic monovalent
saturated hydrocarbon group unless otherwise specified. The same applies to the alkyl
group in an alkoxy group.

The term “alkylene group” includes a linear, branched chain-like, or cyclic
15 divalent saturated hydrocarbon group unless otherwise specified.

The term “halogenated alkyl group” indicates a group in which some or all
hydrogen atoms of an alkyl group have been substituted with halogen atoms. Examples
of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an
iodine atom.

20 The term “fluorinated alkyl group” or “fluorinated alkylene group” indicates a
group in which some or all hydrogen atoms of an alkyl group or an alkylene group have
been substituted with fluorine atoms.

The term “constitutional unit” indicates a monomer unit constituting a polymer
compound (a resin, a polymer, or a copolymer).

25 The expression “may have a substituent” includes a case where a hydrogen atom

(-H) is substituted with a monovalent group and a case where a methylene (-CH₂-) group is substituted with a divalent group.

The term “light exposure” is a general concept for irradiation with radiation.

[0017]

5 The term “polyimide-based resin” denotes 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.

A porous membrane containing at least one of polyimide and polyamide-imide
10 may be referred to as “polyimide-based resin porous membrane”. A porous membrane containing polyimide may be referred to as “polyimide porous membrane”. A porous membrane containing polyamide-imide may be referred to as “porous polyamide-imide membrane”.

[0018]

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

20 [0019]

(Method for Producing Purified Resist Composition)

The method for producing a purified resist composition according to a first aspect of the present invention includes a step of carrying out filtration through a filter having a porous structure in which adjacent spherical cells communicate with each other
25 (hereinafter, also referred to as “step (i)”). The filter has a porous membrane containing

at least one resin selected from the group consisting of polyimide and polyamide-imide.

The resist composition contains a metal compound (M) and an organic solvent

component (S). The metal compound (M) contains a metal ion of a metal atom of

Group 3 to Group 16 or a metal oxide of the metal atom in the long periodic table, and a

5 bonder that is bonded to the metal ion or the metal oxide. The content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to the total mass of the resist composition.

[0020]

In the step (i), the impurities are reduced by adsorbing an aggregated gel of an
10 organometallic complex to the filter from the resist composition. In this manner, a purified resist composition with reduced impurities in a case of forming a resist film is obtained.

According to such a production method, particularly, since a filter including a porous membrane having a porous structure in which adjacent spherical cells
15 communicate with each other and containing at least one resin selected from the group consisting of polyimide and polyamide-imide is used, an aggregated gel of an organometallic complex, which has been difficult to remove in the related art, is sufficiently removed from the resist composition.

In addition, a metal component as an impurity is also sufficiently removed from
20 the resist composition in the step (i). This metal component may be originally contained in the component constituting the resist composition, but may also be mixed from a resist composition transfer path such as a pipe or a joint of a production 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 production device or the like.

25 [0021]

<Step (i)>

The step (i) is a step of filtering the resist composition through a filter having a porous structure in which adjacent spherical cells communicate with each other.

[0022]

5 <<Filter>>

The filter that is used in the present step has a porous structure in which adjacent spherical cells communicate with each other.

For example, such a filter may be formed of a single substance of a porous membrane in which adjacent spherical cells communicate with each other, or may be a
10 filter in which another filter medium is used together with the porous membrane.

Examples of other filter media include a nylon membrane, a polytetrafluoroethylene membrane, a tetrafluoroethylene / perfluoroalkyl vinyl ether copolymer (PFA) membrane, and a membrane obtained by modifying these membranes.

[0023]

15 In such a filter, regions of the porous membrane before and after a liquid passes therethrough are preferably sealed so that a supply liquid and a filtrate of the resist 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
20 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 filter 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),
25 polyimide, polyamide-imide, or the like).

Examples of the form of the porous membrane in such a filter include a planar shape and a pipe shape in which opposite sides of a 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.

5 [0024]

· In regard to "porous membrane in which adjacent spherical cells communicate with each other"

The "porous membrane in which adjacent spherical cells communicate with each other" provided in such a filter has a communication pore in which adjacent spherical
10 cells communicate with each other.

The communication pore is formed of 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 may include a pore having a shape other than this shape.

15 [0025]

In the present specification, a pore in which almost the entire inner surface of the pore is a curved surface is referred to as "spherical cell" or "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 where fine
20 particles that are used in the method for producing a polyimide-based resin porous membrane described below are substantially spherical.

"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. "Substantially spherical" means that a sphericity defined by a ratio of a
25 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 communicate with each other, the adjacent spherical cells form at least a part of the communication pore.

5 [0026]

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

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

The spherical cell 1a and the spherical cell 1b are adjacent to each other, and a communication 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 filtration target flows through the communication pore 5, for example, in the direction
15 (the arrow direction) from the spherical cell 1a toward the spherical cell 1b.

[0027]

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

The "flow path" is generally formed by the individual "pores" and/or "communication pores" that communicate with each other. The individual pores are formed, for example, by removing individual fine particles present in a polyimide-based resin-fine particle composite membrane in a subsequent step in the method for producing
25 a polyimide-based resin porous membrane described below. In addition, the

communication 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 fine particles in a subsequent step in the method for producing a polyimide-based resin
5 porous membrane described below.

In the porous membrane, a spherical cell and a communication pore in which adjacent spherical cells communicate with each other are formed, and thus the degree of porosity is increased. Further, in the porous membrane, a spherical cell or a communication pore opens on a surface of the porous membrane, and a communication
10 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. In addition, according to the porous membrane, in a case where a filtration target flows through the flow path, foreign substances contained in a filtration target are removed from the filtration target before
15 filtration.

[0028]

Since the porous membrane has a flow path obtained by causing communication pores formed by spherical cells having a curved surface on the inner surface thereof to be continuous, the surface area of the inner surface of the spherical cells is large. As a
20 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 substances that are present in the filtration target are adsorbed by the inner surface of the spherical cell, and the foreign
25 substances are easily removed from the filtration target.

[0029]

It is preferable that the porous membrane has a structure in which spherical cells having an average pore diameter of 20 to 2500 nm communicate with each other. The average pore diameter of the spherical cells is preferably 20 to 2500 nm, more preferably 30 to 1000 nm, and still more preferably 50 to 250 nm.

[0030]

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

In addition, the spherical cell may further have a recessed part on the inner surface thereof. For example, a pore having a pore diameter less 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.

[0031]

Examples of "porous membrane in which adjacent spherical cells communicate with each other" include those containing a resin, which may be substantially formed of only a resin, and include those in which the resin in the entire porous membrane is preferably 95% by mass or greater, more preferably 98% by mass or greater, and still more preferably 99% by mass or greater.

[0032]

The porous membrane contains a polyimide-based resin. A porous membrane containing a polyimide-based resin is excellent in foreign substance removing properties and strength, and stability of lithography characteristics before and after filtration.

The porous membrane contains at least one of polyimide and polyamide-imide

as a resin and preferably at least polyimide. The porous membrane may contain only polyimide as a resin or only polyamide-imide, but it is preferable that the porous membrane contains only polyimide.

[0033]

- 5 It is particularly preferable that in "porous membrane in which adjacent spherical cells communicate with each other", 95% by mass or greater 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 communicate with each other, which contains a polyimide-
10 based resin as the resin, will be described.

[0034]

·· 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 a -NH- bond.

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

[0035]

- 20 In the present specification, "salt type carboxy group" means a group obtained by substituting a hydrogen atom in a carboxy group with a cation component. "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
25 charge in a state of being an intermediate state between the two described above.

In a case where "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 " $-COOM_{1/n}$ ".

[0036]

- 5 Examples of "cation component" include a cation in a case where a compound described as a compound contained in an etching liquid described below 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 cation
- 10 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 such as 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 four R's represent organic groups and may be the same as or different from each other). The organic group as R represents preferably an alkyl group and
- 20 more preferably an alkyl group having 1 to 6 carbon atoms. Examples of the quaternary ammonium cation include $N(CH_3)_4^+$.

[0037]

- 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
5 being dried.

[0038]

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
10 and/or a salt type carboxy group and a -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,
15 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.

[0039]

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

In particular, in the method for producing a polyimide porous membrane described below, in a case where a carboxy group and/or a salt type carboxy group is formed of part of imide bonds in the polyimide, an -NH- bond is also formed
25 substantially at the same time. The total number 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 method for producing a porous polyamide-imide membrane, the total number 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 below.

[0040]

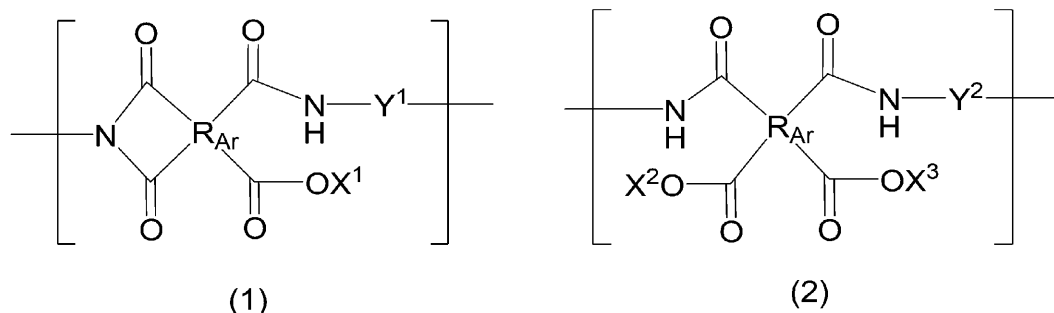
The polyimide-based resin preferably has, for example, at least one constitutional unit selected from the group consisting of constitutional units each represented by General Formulae (1) to (4).

In the case of polyimide, it is preferable to contain at least one 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 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).

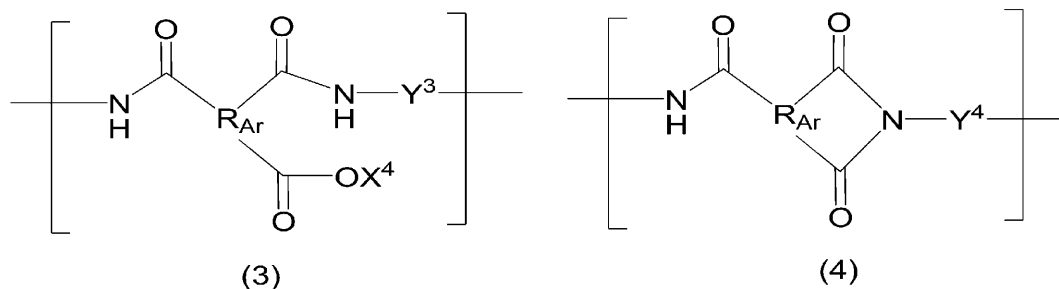
[0041]

[Chemical Formula 1]



[0042]

[Chemical Formula 2]



[0043]

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

R_{Ar} represents an aryl group, and examples thereof include the same groups as those for 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 described below or a constitutional unit represented by General Formula (6) constituting
 10 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 groups as those for 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
 15 described below or a constitutional unit represented by General Formula (6) constituting aromatic polyimide.

[0044]

The polyimide-based resin may be a resin in which a part of an imide bond ($-N[-C(=O)]_2$) of typical polyimide or polyamide-imide is decyclized and has each of the
 20 constitutional unit represented by General Formula (1) or General Formula (2) in a case of polyimide and the constitutional unit represented by General Formula (3) in a case of

polyamide-imide.

[0045]

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.

[0046]

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

10 Procedure (1): For a polyimide-based resin porous membrane that does not undergo the etching (the decyclization of imide bond) step described below (however, in case where a varnish for producing the porous membrane contains a polyamic acid, it is 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 transform infrared spectroscopy (FT-IR) apparatus, to determine a value (X01).

20 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 below, 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 value (X02).

25

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

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

[0047]

5 The non-change rate in the polyimide-based resin porous membrane is preferably in a range of 60% or greater, more preferably in a range of 70% to 99.5%, and 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 a -NH- bond is contained.

10 [0048]

In the case of a polyimide porous membrane, an area of a peak that represents 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”.

15 The imidization rate regarding the value (X02) determined in the above procedure (2) is preferably 1.2 or greater, more preferably in a range of 1.2 to 2, and still 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 greater 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
20 greater.

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

[0049]

25 ·· Method for Producing Polyimide-Based Resin Porous Membrane

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

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

[0050]

 In a case where the resin contained in the polyimide-based resin porous
10 membrane is substantially made of polyamide-imide, the porous membrane already has a -NH- bond even without undergoing the etching step and exhibits good adsorption 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
15 effectively achieving the object of the present invention.

[0051]

 In the method for producing 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
20 as a "polyimide-based resin molded membrane").

 The polyimide-based resin molded membrane to be subjected to the etching step 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 such as a membrane, and it is
25 more preferably porous and has a thin shape such as a membrane from the viewpoint that

the degree of porosity in the polyimide-based resin porous membrane to be obtained can be increased.

[0052]

As described above, the polyimide-based resin molded membrane may be non-
5 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 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]
10 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 polyamide-imide and fine particles, to make the composite membrane porous.

[0053]

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

The production method (a): a method of etching a composite membrane of polyimide and/or polyamide-imide and fine particles before a [fine grain removal] step

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

Among these, the latter production 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.

[0054]

25 An example of the method for producing a polyimide-based resin porous

membrane will be described below.

[0055]

[Preparation of Varnish]

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.

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.

15 [0056]

Resin fine particles are mixed with polyamic acid, or polyimide or polyamide-imide in the varnish 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.

In addition, fine particles are mixed with polyamic acid, or polyimide or polyamide-imide so that the volume fraction 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 formed into a polyimide-based resin-fine particle composite membrane.

25 In a case where the mass ratio or the volume fraction is greater than or equal to

the preferable lower limits of the above-described ranges, pores having a suitable density as a porous membrane can be easily obtained, and in a case where it is less than or equal to than the preferable upper limits of the above-described ranges, problems such as the increase in viscosity and the cracking in the membrane hardly occur, and membrane formation can be stably achieved.

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

[0057]

... Fine Particles

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 materials. 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.

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 be formed in the porous membrane. The organic material is preferably an acrylic resin such as PMMA.

[0058]

The resin fine particles can be selected from, for example, typical linear

polymers and 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

5 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.

[0059]

Among the depolymerizable polymers, from the viewpoint of handling during
10 the formation of pores, 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.

[0060]

15 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.
20 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.

[0061]

The fine particles preferably have a high true sphere ratio since they tend to have
25 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 20 to 2500 nm, more preferably in a range of 30 to 1000 nm, and still more preferably in a range of 50 to 250 nm.

5 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 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.

10 [0062]

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.

15 In a case where the particle diameter distribution index is set to be greater than or equal to the lower limits of the above-described preferable ranges, the porous 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 convections are generated, and thus the adsorption rate of foreign substances is further improved.

20 It is noted that d_{25} and d_{75} are values of particle diameters in which the cumulative frequencies of the particle diameter distribution are each 25% and 75%, and d_{25} is the value having the larger particle diameter in the present specification.

[0063]

Further, in a case of forming an unsintered composite membrane in a two-layer
25 shape in [Membrane formation of unsintered composite membrane] described below, 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.

[0064]

In the present embodiment, a dispersant 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 thus 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 a communication pore that is allowed to be connected to the front and back surfaces of the polyimide-based resin porous membrane, so that 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.

[0065]

As the dispersing agent, a known one can be used without particular limitation.

- 5 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 alkyl
- 10 alkyldiphenyl ether disulfonic acid salt, an alkyl
- 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
- 15 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
- 20 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 polyoxyethylene hydrogenated castor oil, a polyoxyethylene hydrogenated castor oil, a sorbitan lauric acid ester, a polyoxyethylene sorbitan lauric acid ester, and a fatty acid diethanol amide; fatty
- 25 acid alkyl esters such as octyl stearate and trimethylolpropane tridecanoate; and polyether

5 ... Polyamic Acid

[0067]

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.

[0068]

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 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.

10 [0069]

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.

15

[0070]

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 viewpoints of the cost and the availability.

20

The tetracarboxylic acid dianhydride may be used alone, or two or more thereof can be mixed and used.

[0071]

···· Diamine

25

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 in the form of a mixture of two or more kinds thereof.

5 [0072]

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 phenylenediamine or a derivative thereof, a diaminobiphenyl compound or a derivative thereof, a diaminodiphenyl compound or a derivative thereof, a
10 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 fluorinamine derivative.

[0073]

15 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.

[0074]

20 The diaminobiphenyl compound is a compound in which two aminophenyl groups are bonded to each other. Examples of the diaminobiphenyl compound include 4,4'-diaminobiphenyl, and 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl.

[0075]

The diaminodiphenyl compound is a compound obtained by bonding phenyl
25 groups of two aminophenyl groups to each other through another group. 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 more hydrogen atoms of an alkylene group are substituted with a halogen atom or the like.

[0076]

Examples of the diaminodiphenyl compound include 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4, 4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfide, 3,3'-diaminodiphenylketone, 3,4'-diaminodiphenylketone, 2,2-bis(p-aminophenyl)propane, 2,2'-bis(p-aminophenyl)hexafluoropropane, 4-methyl-2,4-bis(p-aminophenyl)-1-pentene, 4-methyl-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'-diaminodiphenylurea, 4,4'-diaminodiphenylamide, 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-aminophenoxy)phenyl]sulphone, bis[4-(3-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane.

[0077]

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

[0078]

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

[0079]

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

10 [0080]

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.

15 [0081]

Examples of the cardo type fluorene amine derivative include 9,9-bisaniline fluorene.

[0082]

20 The aliphatic diamine preferably has, for example, about 2 to 15 carbon atoms, and specific examples thereof include pentamethylenediamine, hexamethylenediamine, and heptamethylenediamine.

[0083]

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

[0084]

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

[0085]

The method for producing a polyamic acid is not particularly limited, and a known technique such as a method of reacting any tetracarboxylic acid 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 solvent can be used alone or in the form of a mixture of two or more kinds thereof.

[0086]

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-diethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, N-methylcaprolactam, 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.

[0087]

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.

5 Further, 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).

10 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.

[0088]

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.

[0089]

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 conditions is preferably in a range of 1,000 to 100,000 centipoises (cP) (1 to 100 Pa·s) and
5 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.

[0090]

... Polyimide

10 As the polyimide that can be used in the present embodiment, any 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.

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
15 during sintering.

[0091]

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

20 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-phenylene, o-tolidine, m-tolidine, 3,3'-dimethoxybenzidine, and 4,4'-diaminobenzanilide; polyoxyalkylenediamines such as polyoxyethylenediamine, polyoxypropylenediamine,
25 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.

[0092]

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.

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

[0093]

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

[0094]

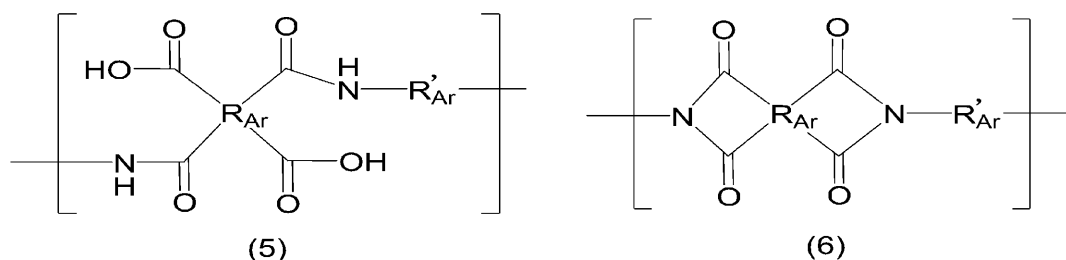
Examples of the polyimide that can be used in the present embodiment include an aliphatic polyimide (a full-aliphatic polyimide) and an aromatic polyimide, and among them, an aromatic polyimide is preferable.

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

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

[0095]

[Chemical Formula 3]



[0096]

In the formulae, R_{Ar} is not particularly limited as long as R_{Ar} represents a cyclic
 5 conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic.
 The number of carbon atoms in the aromatic ring is preferably in a range of 5 to 30, more
 preferably in a range of 5 to 20, still more preferably in a range of 6 to 15, and
 particularly preferably in a range of 6 to 12. Specifically, as the aromatic ring, an
 aromatic hydrocarbon ring such as benzene, naphthalene, anthracene, and phenanthrene;
 10 and an aromatic heterocyclic ring in which some carbon atoms constituting the aromatic
 hydrocarbon ring have been substituted with heteroatoms are exemplary examples.
 Examples of the heteroatom in 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 these, R_{Ar} represents preferably an
 15 aromatic hydrocarbon ring, more preferably benzene or naphthalene, and particularly
 preferably benzene.

In the formulae, examples of R'_{Ar} include a group obtained by removing two
 hydrogen atoms from the aromatic ring as R_{Ar} . Among these, R'_{Ar} represents preferably
 a group obtained by removing two hydrogen atoms from an aromatic hydrocarbon ring,
 20 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 as R_{Ar} and the arylene group as R'_{Ar} may each have a substituent.

[0097]

... Polyamide-Imide

As the polyamide-imide that can be used in the present embodiment, any known
 5 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.

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.

10 [0098]

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.

15 [0099]

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.

[0100]

20 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-isocyanoxidephenoxy)phenyl]sulfone, 2,2'-bis[4-(4-
 isocyanoxidephenoxy)phenyl]propane, 2,4-tolylene diisocyanate, 2,6-tolylene
 25 diisocyanate, 4,4'-diphenylmethane diisocyanate, 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.

[0101]

- 5 Examples of any diamine include the same diamines as those for the diamine described in the section of the polyamic acid above.

[0102]

... Organic Solvent

- 10 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 solvents as those for the organic solvent that is used in the reaction between tetracarboxylic acid dianhydride and a diamine.

- 15 The organic solvent can be used alone or in the form of a mixture of two or more kinds thereof.

[0103]

- 20 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 more preferably in a range of 15% to 40% by mass.

[0104]

- 25 Further, 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 fraction of polyamic acid or polyimide, or a polyamide-imide (A1) to a fine grain (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 the volume occupied by the fine particle (B1) is 55 or greater, 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 the polyimide-based resin molded membrane.

Further, the volume fraction 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, particles are easily dispersed singly and uniformly in a case where the volume occupied by the fine particle (B2) is 50 or greater, and particles 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.

[0105]

Regarding the above-described volume fraction, 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 in a high degree. Further, in a case where a layer having a low fine particle content rate is provided, the production cost can be reduced.

[0106]

In a case of preparing a varnish, in addition to the above-described components, it is possible to blend, as necessary, 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.

[0107]

5 [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 in a range of 1 to 500 μm and more preferably in a range of 5 to 50 μm .

[0108]

15 Here, a mold releasing layer may be provided on the base material as necessary. Further, 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 composite membrane] described below.

20 [0109]

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 known mold releasing agent such as an alkyl phosphate ammonium salt-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 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 method include 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 heated to a suitable set temperature in a constant temperature bath. In this 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.

[0110]

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.

[0111]

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 with the 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 in a range of 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 in a range of 10°C to 90°C).

5 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 in a range of 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 in a range of 10°C to 30°C) to form a second unsintered
10 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.

[0112]

[Sintering of Unsintered Composite Membrane]

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

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

[0113]

The temperature (the sintering temperature) of the heat treatment varies depending on the structure of the polyamic acid, or polyimide or polyamide-imide contained in the unsintered composite membrane and the presence or absence of the
25 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.

[0114]

It is not always necessary to clearly separate the operation from the drying in the previous step in order to perform sintering. For example, in a case of carrying out

5 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 increment) and finally held at 375°C for 20 minutes. At that time, a method in which an
10 end part of the unsintered composite membrane is fixed to a mold made of SUS or the like may be adopted to prevent deformation.

[0115]

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

15 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.

[0116]

20 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.

[0117]

[Fine Particle Removal]

After [Sintering of unsintered composite membrane] described above, the fine
25 particles are removed from the polyimide-based resin-fine particle composite membrane,

whereby a polyimide-based resin porous membrane is produced.

For example, in a case where silica is used as the fine particle, the polyimide-based resin-fine particle composite membrane is brought into contact with a 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 higher than or equal to the thermal decomposition temperature of the resin fine particles and lower than the thermal decomposition temperature of the polyimide-based resin, whereby a porous membrane is obtained.

10 [0118]

[Etching (Decyclization of Imide Bond)]

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

[0119]

15 · In regard to Chemical Etching Method

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

The chemical etching method is not particularly limited, and examples thereof 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 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 amine; tertiary amines such as triethyl amine and methyldiethyl amine; alcohol amines
 5 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.
 [0120]

10 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.
 [0121]

· In regard to Physical Removal Method

15 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.
 [0122]

The above-described chemical etching method or physical removal method can be applied before [Removal of fine particles] described above or can be applied after
 20 [Removal of fine particles] described above.

Among the above, it is preferable to be applied after [Removal of fine particles] described above since the communication pores inside the polyimide-based resin porous membrane are more easily formed and the foreign substance removing property is enhanced.

25 [0123]

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.

5 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.

[0124]

Further, after the etching step, the polyimide-based resin porous membrane may be subjected to heat 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.

[0125]

For example, in the polyimide-based resin porous membrane produced by the above-described production method, spherical cells and a communication pore in which adjacent spherical cells communicate with each other are formed. The polyimide-based resin porous membrane preferably has a communication pore so that a communication 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.

[0126]

The Garley air permeability of the "porous membrane in which adjacent spherical cells communicate with each other" is, for example, preferably 30 seconds or longer 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

25

membrane. The Gurley 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, and particularly preferably in a range of 30 to 500 seconds. In a case where the Gurley air permeability is less than or equal to the above-described preferable ranges, the degree of porosity (the presence ratio of the communication pore and the like) is sufficiently high, and thus the effect of removing foreign substances can be more easily obtained.

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

[0127]

The "porous membrane in which adjacent spherical cells communicate with each other" has communication pores having an average pore diameter of preferably 1 to 1000 nm, more preferably 3 to 300 nm, and still more preferably 5 to 100 nm. The average pore diameter thereof is particularly preferably 10 to 40 nm.

The pore diameter of the communication pore means the diameter of the communication pore. Since one communication pore is usually formed of two adjacent particles by the above-described production method, the diameter may be a diameter in a direction perpendicular to a longitudinal direction in a case where the direction in which two pores constituting the communication pores are adjacent to each other is defined as the longitudinal direction, and thus the pore diameter of the communication pores tends to decrease in a case where the step of (decyclization of an imide bond) is not provided. The average pore diameter of the communication pores of the porous membrane is a value measured by a half-dry method (ASTM E1294-89) with a palm porometer (for example, manufactured by PMI) at a measurement temperature of 25°C and a measurement pressure range of 0 to 400 psi using perfluoropolyester (trade name: Galwick, interfacial tension value: 15.9 dyne/cm) as a reagent.

[0128]

The average pore diameter of "porous membrane in which adjacent spherical cells communicate with each other" is preferably in a range of 20 to 2500 nm, more preferably in a range of 30 to 1000 nm, and still more preferably in a range of 50 to 250

5 nm. Regarding a porous membrane (for example, a porous polyamide-imide membrane) that is not subjected to chemical etching, the average particle diameter of the fine particles that are used in the production of the porous membrane is defined as the average pore diameter of the spherical cells.

[0129]

10 As described above, "porous membrane in which adjacent spherical cells communicate with each other" is preferably a porous membrane containing pores having an average pore diameter of several hundred nanometers. Therefore, for example, even minute substances in the nanometer unit can be adsorbed or captured in the pores and/or the communication pores in the porous membrane.

15 [0130]

Regarding the pore diameter of the communication pore, in a case where the distribution of the pore diameters of the individual pores that impart porosity to "porous membrane in which adjacent spherical cells communicate with each other" is broader, the pore diameter of the communication pore that is formed by pores adjacent to each other
20 tends to decrease.

From the viewpoint of reducing the pore diameter of the communication pores, the void ratio of the "porous membrane in which adjacent spherical cells communicate with 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,
25 and particularly preferably in a range of about 60% to 70% by mass. In a case where

the void ratio is greater than or equal to the above-described lower limits of the above-described ranges, the effect of removing foreign substances can be more easily obtained. In a case where the void ratio is less than or equal to the upper limits of the above-described ranges, the strength of the porous membrane is further increased.

5 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 the like that are used in the production of the porous membrane, and the fine particles. [0131]

 The "porous membrane in which adjacent spherical cells communicate with each
10 other" is excellent in mechanical characteristics such as stress and breaking elongation.

 The stress of the "porous membrane in which adjacent spherical cells communicate with 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.

15 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. [0132]

 Further, the breaking elongation of the "porous membrane in which adjacent
20 spherical cells communicate with each other" is, for example, preferably 10% GL or greater and more preferably 15% GL or greater. The upper limit of the breaking elongation is, 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.

25 The breaking elongation 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.

[0133]

5 The thermal decomposition temperature of "porous membrane in which adjacent spherical cells communicate with each other" is preferably 200°C or higher, more 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.

10 [0134]

The filter in the present embodiment is not limited to the one that includes a porous membrane in which the communication pores 5 in which the adjacent spherical cell 1a and the spherical cell 1b communicate with each other as shown in FIG. 1 is formed, and may include a porous membrane in which, in addition to the communication pores 5, a cell or communication 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 an elliptical cell, a polyhedral cell, a spherical cell having a different pore diameter. Examples of the above-described "communication pore having another form" include a communication pore in which a spherical cell and another cell communicate with each other.

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

25

fine particles, and the like.

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

[0135]

Further, the filter in the present embodiment replaces 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
10 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 (a chemical liquid for lithography) using the same device and operation as those in the related art, and a high-purity purified resist composition can be prepared.

[0136]

15 <<Filtration of Resist Composition>>

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

[0137]

The "state where differential pressure is provided" means that a pressure
25 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 resist composition supply side) of the polyimide-based resin porous membrane, and decompression (negative pressure) that causes one side (the filtrate side) of the

5 polyimide-based resin porous membrane to be negative pressure. In the filtration step according to the present embodiment, the former pressurization is preferable.

[0138]

The pressurization is an operation to apply pressure to the supply liquid side of the polyimide-based resin porous membrane, where a resist composition (hereinafter, 10 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.

15 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.

20 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.

[0139]

For example, in a case where a supply liquid is allowed to pass through the 25 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.

5 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. At that time, the filtrate side where the filtrate has passed through the polyimide-based resin porous membrane may be at
10 atmospheric pressure without being decompressed.

[0140]

Further, the pressurization may utilize both the liquid flow pressure and the positive pressure of the gas. Further, the differential pressure may be a combination of pressurization and decompression, and for example, one that utilizes both liquid flow
15 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
20 preferable from the viewpoint of simplification of production.

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 foreign substance removing property since the polyimide-based resin porous membrane is used.

25 [0141]

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.

5 [0142]

In a case where the operation of allowing the resist 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
10 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.

15 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 of each of the pressure differences is preferably 0.01 MPa or greater and more preferably 0.05 MPa or greater.

20 [0143]

In the step (i), the operation of allowing the resist 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 resist composition (the supply liquid).

25 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 greater, more preferably 3 mL/min or greater, still more preferably 5 mL/min or greater, and particularly preferably 10 mL/min or greater. The upper limit of the flow rate is not particularly limited, and 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 resist composition can be increased.

[0144]

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

[0145]

Further, in the step (i), the resist composition may be allowed to pass through the filter having the polyimide-based resin porous membrane a plurality of times (may be subjected 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.

[0146]

Further, 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.

5 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
10 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 is preferably carried out under pressure particularly in a case where the solution is allowed to permeate into the pores inside the polyimide-based resin porous membrane.
[0147]

15 <Other Steps>

The production 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
20 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
25 filter, a filter having a porous membrane containing a polyethylene resin is preferable

since it is excellent in foreign substance removing property.

[0148]

<<Step (ii)>>

The production method according to the present embodiment preferably further
5 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
10 composed of only a polyethylene resin.

The polyethylene resin porous membrane is not particularly limited, and a
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).

15 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.

[0149]

20 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).

[0150]

25 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 production method according to the present embodiment, the step (ii) may
5 be repeated after the step (i). In this case, the resist 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 performing circulation type filtration as described above, it is preferable that both filters are arranged so that the resist composition passes through the filter having a
10 polyimide-based resin porous membrane and then passes through the filter having a polyethylene resin porous membrane in the circulation path.

[0151]

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
15 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
20 surface energy between the polyethylene resin porous membrane and the supply liquid.

[0152]

<Resist Composition>

The resist composition, which is a filtration target, contains a metal compound (M) and an organic solvent component (S). The metal compound (M) contains a metal
25 ion of a metal atom of Group 3 to Group 16 or a metal oxide of the metal atom in the

long periodic table, and a bonder that is bonded to the metal ion or the metal oxide. The content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to the total mass of the resist composition.

[0153]

5 The resist composition contains a metal compound (M) (hereinafter, also referred to as “component (M)”), and the structure of the metal compound changes upon light exposure, and the solubility of the metal compound in a developing solution changes.

[0154]

10 In a case where a resist film is formed using the resist composition according to the present embodiment and the formed resist film is subjected to selective exposure, the component (M) exhibits changed solubility in a developing solution at exposed portions, whereas the component (M) exhibits unchanged solubility in a developing solution at unexposed portions of the resist film, which generates the difference in solubility in the
15 developing solution between the exposed portion and unexposed portions. Therefore, in a case where the resist film is developed, the exposed portion of the resist film is dissolved and removed to form a positive-tone resist pattern in a case where the resist composition is of a positive-tone, whereas the unexposed portion of the resist film is dissolved and removed to form a negative-tone resist pattern in a case where the resist
20 composition is of a negative tone.

[0155]

 In the present specification, a resist composition which forms a positive-tone resist pattern by dissolving and removing the exposed portion of the resist film is referred to as a positive-tone resist composition, and a resist composition which forms a negative-
25 tone resist pattern by dissolving and removing the unexposed portion of the resist film is

referred to as a negative-tone resist composition. The resist composition according to the present embodiment is typically a negative-tone resist composition. In addition, the resist composition according to the present embodiment may be used for an alkali developing process using an alkali developing solution, or used for a solvent developing process using a developing solution containing an organic solvent (an organic developing solution) in the developing treatment during the pattern formation.

[0156]

[Metal Compound (M)]

The resist composition contains a metal compound (M) (component (M)). The component (M) is a metal compound that contains a metal ion of a metal atom of Group 3 to Group 16 in the long periodic table or a metal oxide of the metal atom, and a bonder that is bonded to the metal ion or the metal oxide. The resist composition contains the component (M) as a base material component. In a case where the component (M) is used, the base material component exhibits changed solubility in an organic solvent before and after exposure, and thus a good development contrast can be obtained in the solvent developing process.

[0157]

In a case where the solvent developing process is applied, the base material component including the component (M) has a high solubility in an organic developing solution before exposure, and the solubility in an organic developing solution decreases upon exposure. Therefore, in a case where selective light exposure is performed on a resist film formed by coating a support with the resist composition in the resist pattern formation, the exposed portion of the resist film is changed from being soluble to being insoluble in an organic developing solution, whereas the unexposed portion of the resist film remains soluble in an organic developing solution. Therefore, a negative-tone

resist pattern is formed by performing development using an organic developing solution so that a contrast is imparted between the exposed portion and the unexposed portion.

[0158]

<<Metal Ion or Metal Oxide ((M1) Component)>>

5 The component (M) contains a metal ion of a metal atom of Group 3 to Group 16 in the long periodic table or a metal oxide of the metal atom (hereinafter, also collectively referred to as “component (M1)”).

[0159]

Examples of the Group 3 metal atom include scandium (Sc) and yttrium (Y).

10 Examples of the Group 4 metal atom include titanium (Ti), zirconium (Zr), and hafnium (Hf).

Examples of the Group 5 metal atom include vanadium (V), niobium (Nb), and tantalum (Ta).

15 Examples of the Group 6 metal atom include chromium (Cr), molybdenum (Mo), and tungsten (W).

Examples of the Group 7 metal atom include manganese (Mn), technetium (Tc), and rhenium (Re).

Examples of the Group 8 metal atom include iron (Fe), ruthenium (Ru), and osmium (Os).

20 Examples of the Group 9 metal atom include cobalt (Co), rhodium (Rh), and iridium (Ir).

Examples of the Group 10 metal atom include nickel (Ni), palladium (Pd), and platinum (Pt).

25 Examples of the Group 11 metal atom include copper (Cu), silver (Ag), and gold (Au).

Examples of the Group 12 metal atom include zinc (Zn), cadmium (Cd), and mercury (g).

Examples of the Group 13 metal atom include aluminum (Al), gallium (Ga), indium (In), and thallium (Tl).

5 Examples of the Group 14 metal atom include germanium (Ga), tin (Sn), and lead (Pb).

Examples of the Group 15 metal atom include antimony (Sb) and bismuth (Bi).

Examples of the Group 16 metal atom include tellurium (Te) and polonium (Po).

[0160]

10 The metal atom is preferably a metal atom of Group 3, Group 4, Group 5, Group 6, Group 13, Group 14, or Group 15, and a metal atom of Group 4 or Group 14 is preferable. As these metal atoms, tin, indium, antimony, molybdenum, vanadium, tantalum, hafnium, zirconia, iron, and niobium are preferable, and tin is more preferable.

[0161]

15 The component (M1) may be a metal ion. The metal ion is not particularly limited as long as it is a metal ion of a metal atom of Group 3 to Group 16 in the long periodic table.

Specific examples of the metal ion include a zirconium ion (Zr^{4+}), a hafnium ion (Hf^{4+}), cobalt (Co^{2+} , Co^{3+}), nickel (Ni^{2+} , Ni^{3+}), zinc (Zn^{2+}), tin (Sn^{2+} , Sn^{4+}), antimony (Sb^{3+}), and tellurium (Te^{4+}), but the present invention is not limited thereto.

20

[0162]

The component (M1) may be a metal oxide of a metal atom of Group 3 to Group 16 in the long periodic table. The metal oxide is a compound formed by covalently bonding a metal atom and oxygen. Examples of the metal oxide include metal oxides of the metal atoms described above.

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Specific examples of the metal atom constituting the metal oxide include the same metal atoms as the metal atoms described above but are not limited to. Specific examples of the metal oxide include metal oxides of Group 3 elements such as scandium oxide (III) (Sc_2O_3) and yttrium oxide (III) (Y_2O_3); metal oxides of Group 4 elements such as titanium oxide (IV) (TiO_2), zirconia (ZrO_2), and hafnium oxide (IV) (HfO_2); metal oxides of Group 5 elements such as vanadium oxide (V) (V_2O_5), niobium oxide (V) (Nb_2O_5), and tantalum oxide (V) (Ta_2O_5); metal oxides of Group 6 elements such as chromium oxide (VI) (CrO_3), molybdenum oxide (VI) (MoO_3), and tungsten oxide (VI) (WO_3); metal oxides of Group 13 elements such as aluminum oxide (III) (Al_2O_3), gallium oxide (III) (Ga_2O_3), and indium oxide (III) (In_2O_3); metal oxides of Group 14 elements such as germanium dioxide (GeO_2), tin oxide (II) (SnO), and tin oxide (IV) (SnO_2); and metal oxides of Group 15 elements such as antimony trioxide (Sb_2O_3), but the present invention is not limited thereto.

In addition, the metal oxide may be a hydroxide of the metal oxide. Examples of the hydroxide of the metal oxide include $\text{Zr}_6\text{O}_4(\text{OH})_4$, $\text{Hf}_6\text{O}_4(\text{OH})_4$, and $\text{Sn}_{12}\text{O}_{14}(\text{OH})_6$, but the present invention is not limited thereto.

[0163]

The component (M1) may be used alone or in combination of two or more kinds thereof.

20 [0164]

<<Bonder ((M2) Component)>>

The component (M) contains a bonder (M2) that is bonded to a metal ion or a metal oxide (hereinafter, also referred to as a “component (M2)”). The bond type between the metal ion or metal oxide and the bonder is not particularly limited and may be any one of a covalent bond, a coordination bond, and an ionic bond.

[0165]

The component (M2) is not particularly limited as long as it can be bonded to a metal ion or a metal oxide. Examples of the bonder include an organic group having 1 to 20 carbon atoms and an inorganic anion.

- 5 The organic group having 1 to 20 carbon atoms has preferably 1 to 15 carbon atoms, more preferably 1 to 12 carbon atoms, and still more preferably 1 to 10 carbon atoms. Examples of the inorganic anion include a hydroxide ion (OH^-), a hydrogen sulfide ion (SH^-), a metaphosphate ion (PO_3^-), and a nitrate ion (NO_3^-).

[0166]

- 10 · Bonder (M2-1) to be Covalently Bonded

Examples of the bonder (hereinafter, also referred to as “bonder (M2-1)”) that is covalently bonded to a metal ion or a metal oxide include an organic group represented by General Formula (m2-1).

[0167]

- 15 [Chemical Formula 4]



- [In the formula, Rm^1 represents a monovalent organic group having 1 to 20 carbon atoms. * represents a bond to a metal ion or a metal oxide. In a case where two or more Rm^1 's that are bonded to a metal ion or a metal oxide are present, the two or
- 20 more Rm^1 's may be bonded to each other to form a di- or higher valent linking group.]

[0168]

In Formula (m2-1), Rm^1 represents a monovalent organic group having 1 to 20 carbon atoms. Examples of the organic group as Rm^1 include a hydrocarbon group having 1 to 20 carbon atoms, which may have a substituent. The hydrocarbon group

has preferably 1 to 15 carbon atoms, more preferably 1 to 10 carbon atoms, still more preferably 1 to 6 carbon atoms, and particularly preferably 1 to 3 carbon atoms. The hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

5 [0169]

The aliphatic hydrocarbon group may be saturated or may be unsaturated. The aliphatic hydrocarbon group may be linear or may be branched.

The linear saturated aliphatic hydrocarbon group is preferably an alkyl group having 1 to 15 carbon atoms, more preferably an alkyl group having 1 to 10 carbon
10 atoms, still more preferably an alkyl group having 1 to 6 carbon atoms, and particularly preferably an alkyl group having 1 to 3 carbon atoms.

The linear unsaturated aliphatic hydrocarbon group is preferably an alkenyl group or alkynyl group having 2 to 15 carbon atoms, more preferably an alkenyl group or alkynyl group having 2 to 10 carbon atoms, still more preferably an alkenyl group or
15 alkynyl group having 2 to 6 carbon atoms, and particularly preferably an alkenyl group or alkynyl group having 2 or 3 carbon atoms.

[0170]

The branched saturated aliphatic hydrocarbon group is preferably a branched alkyl group having 3 to 15 carbon atoms, more preferably a branched alkyl group having
20 3 to 10 carbon atoms, still more preferably a branched alkyl group having 3 to 6 carbon atoms, and particularly preferably a branched alkyl group having 3 to 4 carbon atoms.

The branched unsaturated aliphatic hydrocarbon group is preferably a branched alkenyl group or alkynyl group having 3 to 15 carbon atoms, more preferably a branched alkenyl group or alkynyl group having 3 to 10 carbon atoms, still more preferably a
25 branched alkenyl group or alkynyl group having 3 to 6 carbon atoms, and particularly

preferably a branched alkenyl group or alkynyl group having 3 or 4 carbon atoms.

[0171]

The aliphatic hydrocarbon group may contain a ring in the structure thereof.

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof

5 include a cyclic aliphatic hydrocarbon group which may have a substituent containing a hetero atom in the ring structure thereof (a group obtained by removing two hydrogen atoms from an aliphatic hydrocarbon ring), a group obtained by bonding the cyclic aliphatic hydrocarbon group to the terminal of a linear or branched aliphatic hydrocarbon group, and a group obtained by interposing the cyclic aliphatic hydrocarbon group in a
10 linear or branched aliphatic hydrocarbon group. The number of carbon atoms of the branched aliphatic hydrocarbon group is preferably 3 to 15, more preferably 3 to 10, and still more preferably 3 to 6. The cyclic aliphatic hydrocarbon group may be polycyclic or may be monocyclic.

As the aliphatic hydrocarbon group which is a monocyclic group, a group in

15 which one hydrogen atom has been removed from a monocycloalkane is preferable.

The monocycloalkane has preferably 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

As the aliphatic hydrocarbon group which is a polycyclic group, a group in

which one hydrogen atom has been removed from a polycycloalkane is preferable. As

20 the polycycloalkane, a group having 7 to 12 carbon atoms is preferable, and specific examples thereof include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

[0172]

The organic group as Rm^1 may be an aromatic hydrocarbon group. The

25 aromatic hydrocarbon group is a hydrocarbon group having at least one aromatic ring.

The aromatic ring is not particularly limited as long as the aromatic ring is a cyclic conjugated system having $(4n + 2) \pi$ electrons and may be monocyclic or polycyclic. The number of carbon atoms in the aromatic ring is preferably 5 to 20, more preferably 6 to 15, and still more preferably 6 to 12.

5 Specifically, as the aromatic ring, an aromatic hydrocarbon ring such as benzene, naphthalene, anthracene, and phenanthrene; and an aromatic heterocyclic ring in which some carbon atoms constituting the aromatic hydrocarbon ring have been substituted with heteroatoms are exemplary examples. Examples of the heteroatom in the aromatic heterocyclic rings include an oxygen atom, a sulfur atom, and a nitrogen
10 atom. Specific examples of the aromatic heterocyclic ring include a pyridine ring and a thiophene ring.

Specific examples of the aromatic hydrocarbon group include a group obtained by removing one hydrogen atom from the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring (an aryl group or a heteroaryl group); a group obtained by
15 removing one hydrogen atom from an aromatic compound having two or more aromatic rings (for example, biphenyl or fluorene); and a group obtained by substituting one hydrogen atom of the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring with an alkylene group (for example, an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a
20 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group bonded to the aromatic hydrocarbon ring or the aromatic heterocyclic ring has preferably 1 to 4 carbon atoms, more preferably 1 to 3 carbon atoms, and particularly preferably 1 to 2 carbon atoms.

[0173]

25 The hydrocarbon group as Rm^1 may have a substituent. The substituent may

be a substituent that is substituted for a hydrogen atom (-H) of a hydrocarbon chain or may be a substituent that is substituted for a methylene group (-CH₂-) of a hydrocarbon chain.

5 Examples of the group that is substituted for a hydrogen atom include a carboxy group, a hydroxy group, an amino group, a sulfo group, a nitro group, a thiol group, a cyano group, a phosphoric acid group, a halogen atom, an alkoxy group, and an acyl group, but are not limited thereto. The alkoxy group and the acyl group as the substituent have preferably 1 to 6 carbon atoms, more preferably 1 to 3 carbon atoms, and still more preferably 1 or 2 carbon atoms.

10 Examples of the group that is substituted for a methylene group include -O-, -C(=O)-O-, -O-C(=O)-, -C(=O)-, -O-C(=O)-O-, -C(=O)-NH-, -NH-C(=O)-, -NH-, -S-, -S(=O)₂-, and -S(=O)₂-O-, but are not limited thereto.

[0174]

Rm¹ represents preferably a hydrocarbon group, preferably an aliphatic hydrocarbon group, more preferably a linear or branched aliphatic hydrocarbon group, and still more preferably a branched saturated aliphatic hydrocarbon group. The saturated aliphatic hydrocarbon group is preferably an alkyl group having 1 to 15 carbon atoms, more preferably an alkyl group having 1 to 10 carbon atoms, still more preferably an alkyl group having 1 to 6 carbon atoms, and particularly preferably an alkyl group having 1 to 3 carbon atoms. Specific examples of Rm¹ include a branched alkyl group having 1 to 15 carbon atoms (for example, a t-butyl group), a linear unsaturated hydrocarbon group having 2 to 15 carbon atoms (for example, a vinyl group), a linear alkyl group having 1 to 15 carbon atoms (for example, a methyl group, an ethyl group, or an n-butyl group), and an aromatic hydrocarbon group having 6 to 15 carbon atoms (for example, a phenyl group). Among these, a branched alkyl group having 1 to 15 carbon

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atoms (for example, a t-butyl group), a linear unsaturated hydrocarbon group having 2 to 15 carbon atoms (for example, a vinyl group), or a linear alkyl group having 1 to 15 carbon atoms (for example, a methyl group, an ethyl group, or an n-butyl group) is preferable, a branched alkyl group having 1 to 15 carbon atoms (for example, a t-butyl group) or a linear unsaturated hydrocarbon group having 2 to 15 carbon atoms (for example, a vinyl group) is more preferable, and a branched alkyl group having 1 to 15 carbon atoms (for example, a t-butyl group) is still more preferable.

[0175]

In a case where two or more bonders (M2-1) that are bonded to a metal ion or a metal oxide are present, two or more Rm^1 's contained in the two or more bonders (M2-1) may be bonded to each other to form a di- or higher valent linking group.

[0176]

The bonder (M2-1) may be used alone or in combination of two or more kinds thereof.

15 [0177]

· Bonder (M2-2) to be Coordinately Bonded

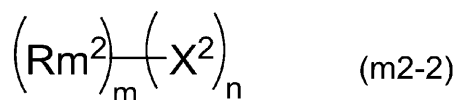
Examples of the bonder (hereinafter, also referred to as “bonder (M2-2)”) that is coordinately bonded to a metal ion or metal oxide include an organic anion or an inorganic anion.

20 Examples of the inorganic anion include a hydroxide ion (OH^-), a hydrogen sulfide ion (SH^-), a metaphosphate ion (PO_3^-), and a nitrate ion (NO_3^-).

Examples of the organic anion include an organic anion represented by General Formula (m2-2).

[0178]

25 [Chemical Formula 5]



[In the formula, Rm^2 represents an organic group. X^2 represents an anionic group. m represents an integer of 0 to 3. n represents an integer of 1 to 4. In a case where n/m is 2 or greater, a plurality of Rm^2 's may be the same as or may be different from each other. In a case where n/m is 2 or greater, a plurality of X^2 's may be the same as or may be different from each other.]

[0179]

In Formula (m2-2), Rm^2 represents an organic group. Examples of the organic group include a hydrocarbon group which may have a substituent. Examples of the hydrocarbon group include a group described as a monovalent hydrocarbon group as Rm^1 in Formula (m2-1), a group obtained by removing one hydrogen atom from the group described as a monovalent hydrocarbon group as Rm^1 in Formula (m2-1), a group obtained by removing two hydrogen atoms from the group described as a monovalent hydrocarbon group as Rm^1 in Formula (m2-1), and a group obtained by removing three hydrogen atoms from the group described as a monovalent hydrocarbon group as Rm^1 in Formula (m2-1). Preferred examples thereof include a group obtained by removing 1 to 3 hydrogen atoms from the group of the preferred example, described as the monovalent hydrocarbon group as Rm^1 in Formula (m2-1).

[0180]

The hydrocarbon group as Rm^2 may have a substituent. Examples of the substituent include the same groups as those for the substituent as Rm^1 in General Formula (m2-1).

The group that is substituted for a hydrogen atom is preferably a cyano group, a nitro group, a halogen atom, an alkoxy group, or an acyl group. The alkoxy group and

the acyl group as the substituent have preferably 1 to 6 carbon atoms, more preferably 1 to 3 carbon atoms, and still more preferably 1 or 2 carbon atoms.

Examples of the group that is substituted for a methylene group include -O-, -C(=O)-O-, -O-C(=O)-, -C(=O)-, -O-C(=O)-O-, -C(=O)-NH-, -NH-C(=O)-, -NH-, -S-, -S(=O)₂-, and -S(=O)₂-O-, but are not limited thereto.

[0181]

m represents an integer of 0 to 3.

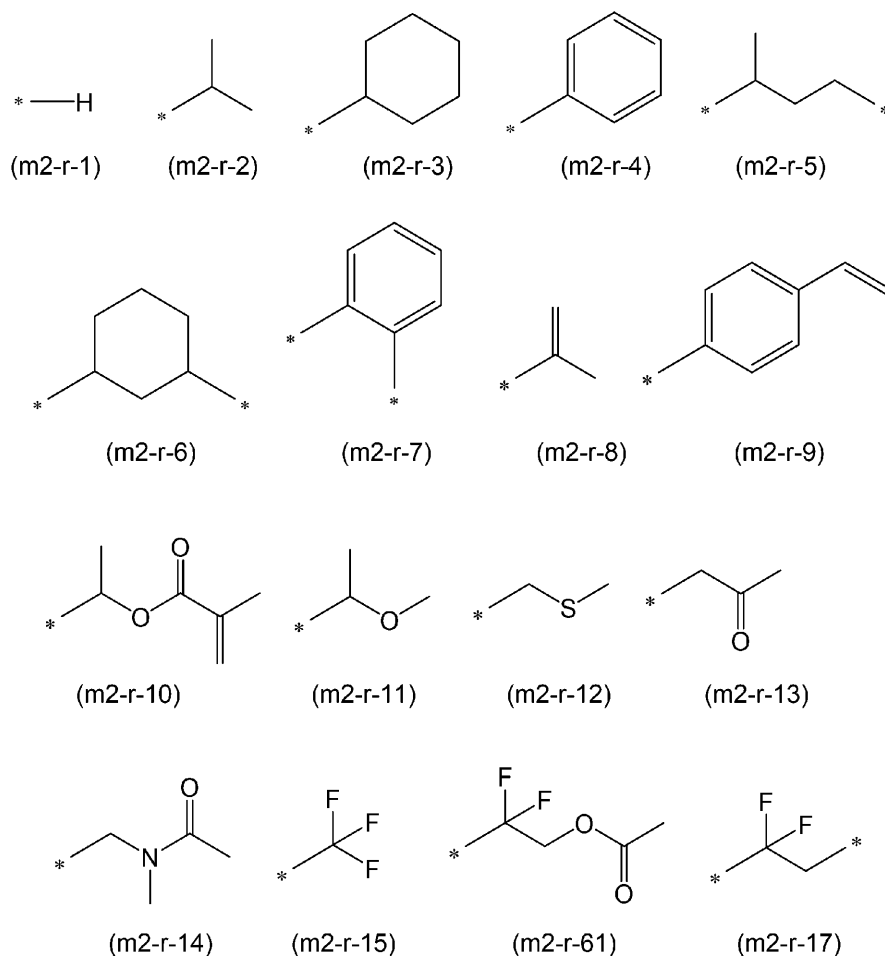
n represents an integer of 1 to 4. In a case where m is 1, n is preferably in a range of 1 to 3 and more preferably 1 or 2. In a case where m is 2 or 3, n is preferably 1.

[0182]

Specific examples of Rm² are shown below, but are not limited thereto. In the formulae, * represents a bond to X² in Formula (m2-2).

[0183]

15 [Chemical Formula 6]



[0184]

In Formula (m2-2), X^2 represents an m/n-valent anionic group. The anionic group is a functional group containing a negatively charged atom. It is preferable that

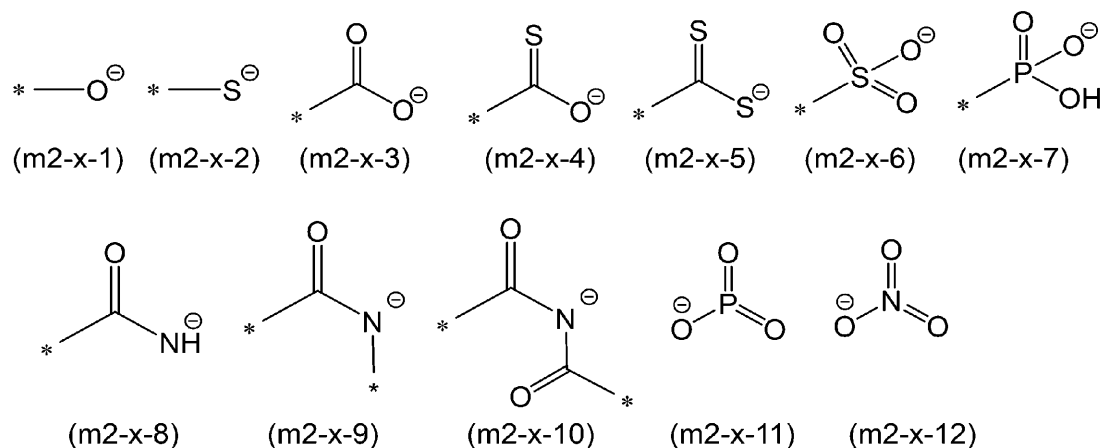
5 X^2 represents an anionic group including $-\text{O}^-$, $-\text{S}^-$, $-\text{SO}^-$, $-\text{SS}^-$, SO_3^- , $\text{P}(\text{OH})\text{O}_3^-$, $-\text{NH}^-$, or $-\text{N}^--\text{CO}-$.

[0185]

Specific examples of X^2 are shown below, but are not limited thereto. In the formulae, * represents a bond to Rm^2 in Formula (m2-2).

10 [0186]

[Chemical Formula 7]

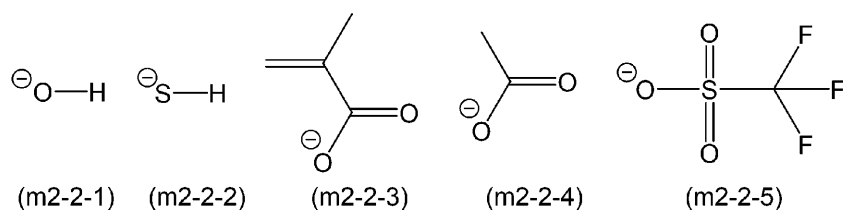


[0187]

Specific examples of the bonder (M2-2) are shown below, but are not limited thereto.

5 [0188]

[Chemical Formula 8]



[0189]

The bonder (M2-2) may be used alone or in combination of two or more kinds thereof.

[0190]

· Bonder (M2-3) to be Ionically Bonded

Examples of the bonder (hereinafter, also referred to as “bonder (M2-3)”) that is ionically bonded to a metal ion or metal oxide include an organic anion or an inorganic anion. Examples of the organic anion and the inorganic anion include the same anions as those for the organic anions and the inorganic anions described in the bonder (M2-2).

[0191]

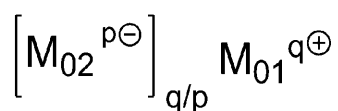
The bonder (M2-3) may be used alone or in combination of two or more kinds thereof.

[0192]

- 5 In a case where the component (M2) is the bonder (M2-3), the component (M1) is a metal ion of a metal atom of Group 3 to Group 16 in the long periodic table. An example of the component (M) in a case where the component (M2) is the bonder (M2-3) is shown below.

[0193]

- 10 [Chemical Formula 9]



[In the formula, M_{01} represents a p-valent cation of a metal atom in Group 3 to Group 16 in the long period table, and M_{02} represents a bonder (M2) which is a p-valent anion.]

- 15 [0194]

- The proportion of the component (M2) with respect to the component (M1) is preferably in a range of 10 to 900 parts by mass, more preferably in a range of 30 to 400 parts by mass, and still more preferably in a range of 30 to 200 parts by mass, with respect to 100 parts by mass of the (M1) component. The molar ratio of the component
- 20 (M1) to the component (M2) ((M1) component:(M2) component (molar ratio)) is preferably in a range of 1:1 to 1:20, more preferably in a range of 1:4 to 1:14, and still more preferably in a range of 1:12 to 1:14. In a case where the ratio of the component (M1) to the component (M2) is set to be in the above-described preferable ranges, the stability of the resist composition is improved.

[0195]

The content of the metal atom in the component (M) is preferably in a range of 10% to 80% by mass, more preferably in a range of 20% to 70% by mass, and still more preferably in a range of 30% to 60% by mass. In a case where the content of the metal atom in the component (M) is set to be in the above-described preferable ranges, the stability of the resist composition is improved.

[0196]

In the resist composition according to the present embodiment, the content of the metal atom (hereinafter, also referred to as a "content of the metal atom") contained in the metal ion or the metal oxide is in a range of 0.2% to 3% by mass with respect to the total mass (100% by mass) of the resist composition. The content of the metal atom is preferably 0.4% to 3.0% by mass, more preferably 0.4% to 2.0% by mass, and still more preferably 0.4% to 1.7% by mass. In a case where the content of the metal atom is within the above range, the function as a negative-tone resist composition is exhibited.

The content of the metal atom with respect to the total mass (100% by mass) of the resist composition can be calculated by the following expression.

Content of metal atom (% by mass) = [(content of metal atom with respect to total mass of component (M) (% by mass)) × (total mass of component (M))]/(total mass of resist composition)

[0197]

In the expression above, "content of metal atom (% by mass) with respect to total mass of component (M)" can be calculated based on the mass of the metal oxide remaining after the component (M) is heated at 600°C and the mass of the component (M) subject to the heating.

[0198]

The metal compound of the component (M) can be produced by using a known method.

For example, the metal compound of the component (M) can be obtained by reacting a metal alkoxide of the metal constituting the component (M1) with the component (M2) in an appropriate solvent. As the solvent, for example, an alcohol-based solvent, a ketone-based solvent, an amide-based solvent, an ether-based solvent, an ester-based solvent, or a hydrocarbon-based solvent can be used. Specific examples of these solvents include solvents described in the component (S) described below.

Examples of the reaction temperature include 0°C to 150°C, and 10°C to 120°C is preferable. Examples of the reaction time include 30 minutes to 24 hours, and 1 to 20 hours are preferable.

[0199]

<Organic Solvent Component (S)>

The resist composition can be produced by dissolving the resist materials in an organic solvent component (hereinafter, referred to as “component (S)”).

The component (S) may be any organic solvent that can dissolve or disperse each of the components to be used to obtain a homogeneous solution or a dispersion liquid, and optional organic solvent can be appropriately selected and used from those which are known as solvents for a resist composition in the related art.

Examples of the component (S) include lactones such as γ -butyrolactone; ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl-n-pentyl ketone, and methyl isopentyl ketone, 2-heptanone; monoalcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, t-butanol, n-pentanol, 4-methyl-2-pentanol, and 2-methylbutyl alcohol; polyhydric alcohols, such as ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol; compounds having an ester

bond, such as ethylene glycol monoacetate, diethylene glycol monoacetate, propylene glycol monoacetate, and dipropylene glycol monoacetate; polyhydric alcohol derivatives including compounds having an ether bond, such as a monoalkyl ether (such as monomethyl ether, monoethyl ether, monopropyl ether or monobutyl ether) or

5 monophenyl ether of any of these polyhydric alcohols or compounds having an ester bond [among these, propylene glycol monomethyl ether acetate (PGMEA) and propylene glycol monomethyl ether (PGME) are preferable]; 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;

10 aromatic organic solvents such as anisole, ethyl benzyl ether, cresyl methyl ether, diphenyl ether, dibenzyl ether, phenetole, butyl phenyl ether, ethyl benzene, diethyl benzene, pentyl benzene, isopropyl benzene, toluene, xylene, cymene and mesitylene; and dimethylsulfoxide (DMSO).

In the resist composition of the present embodiment, the component (S) may be

15 used alone or in the form of a mixed solvent of two or more kinds thereof. Among these, PGMEA, PGME, γ -butyrolactone, EL, cyclohexanone, 4-methyl-2-pentanol, and n-propanol are preferable.

[0200]

Further, a mixed solvent obtained by mixing PGMEA with a polar solvent is also

20 preferable as the component (S). The blending ratio (mass ratio) of the mixed solvent can be appropriately determined in consideration of the compatibility between PGMEA and the polar solvent, but is preferably in the range of 1:9 to 9:1 and more preferably in a range of 2:8 to 8:2.

More specifically, in a case where EL or cyclohexanone is blended as the polar

25 solvent, the mass ratio of PGMEA to EL or cyclohexanone is preferably in a range of 1:9

to 9:1 and more preferably in a range of 2:8 to 8:2. Further, in a case where PGME is blended as the polar solvent, the mass ratio of PGMEA to PGME is preferably in a range of 1:9 to 9:1, more preferably in a range of 2:8 to 8:2, and still more preferably in a range of 3:7 to 7:3. Further, a mixed solvent of PGMEA, PGME, and cyclohexanone is also
5 preferable.

Further, a mixed solvent of γ -butyrolactone and at least one selected from PGMEA and EL is also preferable as the component (S). In this case, as the mixing ratio, the mass ratio between the former and the latter is preferably in a range of 70:30 to 95:5.

10 The amount of the component (S) to be used is not particularly limited and is appropriately set to have a concentration which enables coating a substrate or the like depending on the thickness of the coated film. The component (S) is typically used in an amount such that the solid content concentration of the resist composition is set to be in a range of 0.1% to 20% by mass and preferably in a range of 0.2% to 15% by mass.

15 [0201]

<Other Components>

The resist composition may contain other components in addition to the component (M) and the component (S).

[0202]

20 [Crosslinking Accelerator]

The resist composition may contain a crosslinking accelerator. A crosslinking accelerator is a compound that generates acid or base by light or heat. In a case where a crosslinking accelerator is contained, resist pattern forming properties and etching selectivity can be improved. Examples of the crosslinking accelerator include an onium salt compound and an N-sulfonyloxyimide compound. The crosslinking accelerator is
25

preferably a thermal crosslinking accelerator that generates acid or a base by heat, and an onium salt compound is particularly preferable.

[0203]

Examples of the onium salt compound include a sulfonium salt, a
 5 tetrahydrothiophenium salt, an iodonium salt, and an ammonium salt.

[0204]

Examples of the sulfonium salt include triphenylsulfonium
 trifluoromethanesulfonate, triphenylsulfonium nonafluoro-n-butanesulfonate,
 triphenylsulfonium perfluoro-n-octanesulfonate, triphenylsulfonium 2-
 10 bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate, 4-
 cyclohexylphenyldiphenylsulfonium trifluoromethanesulfonate, 4-
 cyclohexylphenyldiphenylsulfonium nonafluoro-n-butanesulfonate, 4-
 cyclohexylphenyldiphenylsulfonium perfluoro- n-octanesulfonate, 4-
 cyclohexylphenyldiphenylsulfonium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-
 15 tetrafluoroethanesulfonate, 4-methanesulfonylphenyldiphenylsulfonium
 trifluoromethanesulfonate, 4-methanesulfonylphenyldiphenylsulfonium nonafluoro-n-
 butanesulfonate, 4-methanesulfonylphenyldiphenylsulfonium perfluoro-n-
 octanesulfonate, 4-methanesulfonylphenyldiphenylsulfonium 2-bicyclo[2.2.1]hept-2-yl-
 1,1,2,2-tetrafluoroethanesulfonate, and triphenylsulfonium 1,1,2,2-tetrafluoro-6-(1-
 20 adamantancarbonyloxy)-hexane-1-sulfonate.

[0205]

Examples of the tetrahydrothiophenium salt include 1-(4-n-butoxynaphthalene-
 1-yl)tetrahydrothiophenium trifluoromethanesulfonate, 1-(4-n-butoxynaphthalene-1-
 1-yl)tetrahydrothiophenium nonafluoro-n-butanesulfonate, 1-(4-n-butoxynaphthalene-1-
 25 yl)tetrahydrothiophenium perfluoro-n-octanesulfonate, 1-(4-n-butoxynaphthalene-1-

- yl)tetrahydrothiophenium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate, 1-(6-n-butoxynaphthalene-2-yl)tetrahydrothiophenium trifluoromethanesulfonate, 1-(6-n-butoxynaphthalene-2-yl)tetrahydrothiophenium nonafluoro-n-butanesulfonate, 1-(6-n-butoxynaphthalene-2-yl)tetrahydrothiophenium perfluoro-n-octanesulfonate, 1-(6-n-butoxynaphthalene-2-yl)tetrahydrothiophenium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate, 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium trifluoromethanesulfonate, 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium nonafluoro-n-butanesulfonate, 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium perfluoro-n-octanesulfonate, and 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate.

[0206]

- Examples of the iodonium salt include diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoro-n-butanesulfonate, diphenyliodonium perfluoro-n-octanesulfonate, diphenyliodonium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate, bis(4-t-butylphenyl)iodonium trifluoromethanesulfonate, bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate, bis(4-t-butylphenyl)iodonium perfluoro-n-octanesulfonate, and bis(4-t-butylphenyl)iodonium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate.

[0207]

- Examples of the ammonium salt include ammonium formate, ammonium maleate, ammonium fumarate, ammonium phthalate, ammonium malonate, ammonium succinate, ammonium tartrate, ammonium malate, ammonium lactate, ammonium citrate, ammonium acetate, ammonium propionate, ammonium butanoate, ammonium pentanoate, ammonium hexanoate, ammonium heptanoate, ammonium octanoate,

ammonium nonanoate, ammonium decanoate, ammonium oxalate, ammonium adipate, ammonium sebacate, ammonium butyrate, ammonium oleate, ammonium stearate, ammonium linoleate, ammonium linolenate, ammonium salicylate, ammonium benzenesulfonate, ammonium benzoate, ammonium p-aminobenzoate, ammonium p-toluenesulfonate, ammonium methanesulfonate, ammonium trifluoromethanesulfonate, and ammonium trifluoroethanesulfonate. In addition, examples thereof include an ammonium salt in which the ammonium ion of the above ammonium salt is substituted with a methylammonium ion, a dimethylammonium ion, a trimethylammonium ion, a tetramethylammonium ion, an ethylammonium ion, a diethylammonium ion, a triethylammonium ion, a tetraethylammonium ion, a propylammonium ion, a dipropylammonium ion, a tripropylammonium ion, a tetrapropylammonium ion, a butylammonium ion, a dibutylammonium ion, a tributylammonium ion, a tetrabutylammonium ion, a trimethylethylammonium ion, a dimethyldiethylammonium ion, a dimethylethylpropylammonium ion, a methylethylpropylbutylammonium ion, an ethanolammonium ion, a diethanolammonium ion, or a triethanolammonium ion; a 1,8-diazabicyclo[5.4.0]undec-7-ene salt such as a 1,8-diazabicyclo[5.4.0]undec-7-ene formic acid salt or a 1,8-diazabicyclo[5.4.0]undec-7-ene p-toluenesulfonic acid salt; and a 1,5-diazabicyclo[4.3.0]-5-nonene salt such as a 1,5-diazabicyclo[4.3.0]-5-nonene formic acid salt or a 1,5-diazabicyclo[4.3.0]-5-nonene p-toluenesulfonate.

[0208]

Examples of the N-sulfonyloxyimide compound include N-(trifluoromethanesulfonyloxy)bicyclo[2.2.1]hept-5-en-2,3-dicarboxyimide, N-(nonafluoro-n-butanesulfonyloxy)bicyclo[2.2.1]hept-5-en-2,3-dicarboxyimide, N-(perfluoro-n-octanesulfonyloxy)bicyclo[2.2.1]hept-5-en-2,3-dicarboxyimide, and N-(2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonyloxy)bicyclo[2.2.1]hept-5-en-

2,3-dicarboxyimide.

[0209]

Among these, an onium salt compound is preferable, a tetrahydrothiophenium salt, an iodonium salt, or an ammonium salt is more preferable, and 1-(4-n-

5 butoxynaphthalen-1-yl)tetrahydrothiophenium trifluoromethanesulfonate, diphenyliodonium trifluoromethanesulfonate, tetramethylammonium acetate, or 1,8-diazabicyclo[5.4.0]undec-7-enep-toluenesulfonate is still more preferable.

[0210]

The crosslinking accelerator may be used alone or in combination of two or
10 more kinds thereof. The content of the crosslinking accelerator is preferably 0 parts by mass or more and 10 parts by mass or less, and more preferably 0 parts by mass or more and 5 parts by mass or less, with respect to 100 parts by mass of the component (M).

[0211]

[Surfactant]

15 The resist composition may contain a surfactant.

The surfactant is a component that exhibits effects of improving coatability, striation. In addition to nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene n-octylphenyl ether, polyoxyethylene n-nonylphenyl ether, polyethylene glycol dilaurate,
20 and polyethylene glycol distearate, examples of the surfactant include, as the following product names, KP341 (Shin-Etsu Chemical Co., Ltd.); Polyflow No. 75 and Polyflow No. 95 (all manufactured by Kyoeisha Chemical Co., Ltd.); Eftop EF301, Eftop EF303, and Eftop EF352 (all manufactured by Tochem Products Co., Ltd.); MEGAFACE F171, MEGAFACE F173 (all manufactured by DIC Corporation); Florard FC430 and Florard
25 FC431 (all manufactured by Sumitomo 3M Limited); and AsahiGuard AG710, Surflon S-

382, Surflon SC-101, Surflon SC-102, Surflon SC-103, Surflon SC-104, Surflon SC-105, and Surflon SC-106 (all manufactured by AGC Inc.).

[0212]

The surfactant may be used alone or in combination of two or more kinds thereof. The blending amount of the surfactant can be appropriately determined depending on the intended purpose.

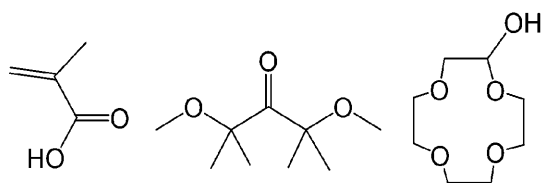
[0213]

[Other Additives]

The resist composition may contain additives other than the crosslinking accelerator and the surfactant. Examples of the other additive include, but are not limited to, the following compounds.

[0214]

[Chemical Formula 10]



15 [0215]

According to the method for producing a purified resist composition of the present aspect described above, a filtration target (a resist composition) is filtered in the step (i) by using a filter having a porous membrane that has a porous structure in which adjacent spherical cells communicate with each other and contains at least one resin skeleton selected from the group consisting of polyimide and polyamide-imide. As a result, foreign substances such as an organic substance and a metal impurity are removed from the filtration target more than ever.

In the resist composition including the metal compound (M), the metal suboxide

or the metal hydroxide constituting the metal compound (M) tends to aggregate to form a gel. In addition, ionic impurities derived from the metal compound (M) may be generated.

In the production method the present embodiment, various impurities such as an aggregated gel derived from the metal compound (M) and an ionic impurity derived from the metal compound (M) are sufficiently removed by performing filtration using a polyimide-based resin porous membrane. Therefore, a high-purity purified resist composition which can reduce the occurrence of defects in a case of forming a resist film can be obtained by such a production method.

10 [0216]

The filter in the present aspect is not limited to the one that includes a porous membrane in which the communication pores 5 in which the adjacent spherical cell 1a and the spherical cell 1b communicate with each other as shown in FIG. 1 is formed, and may include a porous membrane in which, in addition to the communication pores 5 in which the spherical cells 1a and 1b communicate with each other, a cell or communication 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 an elliptical cell, a polyhedral cell, a spherical cell having a different pore diameter. Examples of the above-described "communication pore having another form" include a communication pore in which a spherical cell and another cell communicate with each other.

The shape or pore diameter of another cell may be appropriately determined depending on the kinds of impurities to be removed. The communication pore in which a spherical cell and another cell communicate with each other can be formed, for

example, by selecting a material of the fine particle material described above or controlling the shape of the fine particles.

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

[0217]

Further, the filter having a polyimide-based resin porous membrane, which is 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 resist 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 high-purity purified resist composition can be produced.

[0218]

(Method for Forming Resist Pattern)

The method for forming a resist pattern according to the second aspect of the present invention includes a step of obtaining a purified resist composition, by the method for producing a purified resist composition according to the first aspect, a step of forming a resist film on a support using the purified resist composition, a step of exposing the resist film, and a step of developing the exposed resist film to form a resist pattern.

[0219]

The method for forming a resist pattern according to the present aspect can be

carried out, for example, as follows.

First, a purified resist composition is obtained by the method for producing a purified resist composition according to the first aspect.

Next, the purified resist composition is applied onto a support with a spinner or
5 the like, and subjected to a bake (post apply bake (PAB)) treatment, for example, under a temperature condition of 80°C to 200°C for 40 to 120 seconds and preferably for 60 to 90 seconds to form a resist film.

Following the selective exposure carried out on the resist film by, for example, exposure through a mask (mask pattern) having a predetermined pattern formed on the
10 mask by using an exposure apparatus such as an ArF exposure apparatus, an electron beam lithography apparatus, or an extreme ultraviolet (EUV) exposure apparatus, or direct irradiation of the resist film for drawing with an electron beam without using a mask pattern, a bake treatment (post exposure bake (PEB)) is carried out, for example, under a temperature condition of 80°C to 200°C for 40 to 120 seconds and preferably 60
15 to 90 seconds.

Next, the resist film is subjected to a developing treatment. The developing treatment is performed using an alkali developing solution in a case of the alkali developing process, and the developing treatment is performed using a developing solution (organic developing solution) containing an organic solvent or a mixed solvent
20 of an organic solvent and water in a case of a solvent developing process.

After the developing treatment, it is preferable to conduct a rinse treatment. As the rinse treatment, water rinsing using pure water is preferable in a case of the alkali developing process, and rinsing using a rinse solution containing an organic solvent is preferable in a case of the solvent developing process.

25 In a case of a solvent developing process, after the developing treatment or the

rinse treatment, the developing solution or the rinse liquid remaining on the pattern can be removed by a treatment using a supercritical fluid.

After the developing treatment or the rinse treatment, drying is conducted. As desired, a bake treatment (post-bake) may be conducted after the developing treatment.

5 In this manner, a resist pattern can be formed.

[0220]

The support is not particularly limited and a known support of the related art can be used, and examples thereof include a substrate for an electronic component and a substrate on which a predetermined wiring pattern has been formed. Specific examples
10 thereof include a metal substrate such as a silicon wafer, copper, chromium, iron, or aluminum; and a glass substrate. As the materials of the wiring pattern, copper, aluminum, nickel, or gold can be used.

Further, as the support, any one of the above-described supports provided with an inorganic and/or organic film on the above-described substrate may be used. As the
15 inorganic film, an inorganic antireflection film (inorganic BARC) can be used. As the organic film, an organic film such as an organic antireflection film (organic BARC) or a lower-layer organic film used in a multilayer resist method can be used.

[0221]

The wavelength to be used for light exposure is not particularly limited and the
20 exposure can be conducted using radiation such as an ArF excimer laser, a KrF excimer laser, an F₂ excimer laser, extreme ultraviolet (EUV) rays, vacuum ultraviolet rays (VUV), electron beams (EB), X-rays, and soft X-rays. The purified resist composition is highly useful for a KrF excimer laser, an ArF excimer laser, EB, or EUV, and is particularly useful for EB or EUV.

25 [0222]

The method of exposing the resist film to light can be general exposure (dry exposure) conducted in air or an inert gas such as nitrogen, or liquid immersion exposure (liquid immersion lithography).

5 The liquid immersion lithography is an exposure method in which the region between the resist film and the lens at the lowermost position of the exposure apparatus is pre-filled with a solvent (liquid immersion medium) that has a larger refractive index than the refractive index of air, and the exposure (immersion exposure) is carried out in this state.

10 As the liquid immersion medium, a solvent which has a refractive index larger than the refractive index of air but smaller than the refractive index of the resist film to be exposed to light is preferable. The refractive index of such a solvent is not particularly limited as long as the refractive index is in the above-described range.

15 Examples of the solvent which has a refractive index that is larger than the refractive index of air but smaller than the refractive index of the resist film include water, a fluorine-based inert liquid, a silicon-based solvent, and a hydrocarbon-based solvent.

20 Specific examples of the fluorine-based inert liquid include a liquid containing a fluorine-based compound such as $C_3HCl_2F_5$, $C_4F_9OCH_3$, $C_4F_9OC_2H_5$, or $C_5H_3F_7$ as a main component, and a liquid with a boiling point of 70°C to 180°C is preferable and a liquid with a boiling point of 80°C to 160°C is more preferable. A fluorine-based inert liquid having a boiling point in the above-described range is preferable from the viewpoint that a medium used for liquid immersion can be removed using a simple method after completion of light exposure.

25 As the fluorine-based inert liquid, a perfluoroalkyl compound in which all hydrogen atoms in the alkyl group have been substituted with fluorine atoms is

particularly preferable. Specific examples of the perfluoroalkyl compound include a perfluoroalkylether compound and a perfluoroalkylamine compound.

Further, specific examples of the perfluoroalkylether compound include perfluoro(2-butyl-tetrahydrofuran) (boiling point of 102°C), and specific examples of the
5 perfluoroalkylamine compound include perfluorotributylamine (boiling point of 174°C).

As the liquid immersion medium, water is preferable from the viewpoints of the cost, the safety, the environmental issues, and the versatility.

[0223]

As the alkali developing solution used for the developing treatment in the alkali
10 developing process, a 0.1 to 10 mass% tetramethylammonium hydroxide (TMAH) aqueous solution is an exemplary example.

The organic solvent contained in the organic developing solution used for the developing treatment in the solvent developing process may be any solvent that is capable of dissolving the component (A) (the component (A) before light exposure) and
15 can be appropriately selected from known organic solvents. Specific examples thereof include a polar solvent such as a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, a nitrile-based solvent, an amide-based solvent, and an ether-based solvent, and a hydrocarbon-based solvent.

The ketone-based solvent is an organic solvent containing C-C(=O)-C in the
20 structure thereof. The ester-based solvent is an organic solvent containing C-C(=O)-O-C in the structure thereof. The alcohol-based solvent is an organic solvent containing an alcoholic hydroxyl group in the structure thereof. The term "alcoholic hydroxyl group" indicates a hydroxyl group bonded to a carbon atom of an aliphatic hydrocarbon group. The nitrile-based solvent is an organic solvent containing a nitrile group in the structure
25 thereof. The amide-based solvent is an organic solvent containing an amide group in

the structure thereof. The ether-based solvent is an organic solvent containing C-O-C in the structure thereof.

Some organic solvents have a plurality of the functional groups which characterize each of the solvents in the structure thereof. In such a case, the organic solvents are considered to correspond to all the solvents containing the functional groups. For example, diethylene glycol monomethylether corresponds to both the alcohol-based solvent and the ether-based solvent which have been classified above.

The hydrocarbon-based solvent is a hydrocarbon solvent which is formed of a hydrocarbon that may be halogenated and does not have a substituent other than halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

Among the examples, as the organic solvent contained in the organic developing solution, a polar solvent is preferable. Further, a ketone-based solvent, an ester-based solvent, and a nitrile-based solvent are preferable.

[0224]

Known additives can be blended into the organic developing solution as necessary. Examples of the additive include a surfactant. The surfactant is not particularly limited, and for example, an ionic or non-ionic fluorine-based and/or silicon-based surfactant can be used. As the surfactant, a non-ionic surfactant is preferable, and a non-ionic fluorine-based surfactant or a non-ionic silicon-based surfactant is more preferable.

In a case where a surfactant is blended into the solution, the amount of the surfactant to be blended is typically in a range of 0.001% to 5% by mass, preferably in a range of 0.005% to 2% by mass, and more preferably in a range of 0.01% to 0.5% by mass with respect to the total amount of the organic developing solution.

[0225]

The developing treatment can be performed according to a known developing method, and examples thereof include a method of immersing a support in a developing solution for a certain time (a dip method), a method of raising a developing solution on the surface of a support using the surface tension and maintaining the state for a certain time (a puddle method), a method of spraying a developing solution to the surface of a support (spray method), and a method of continuously ejecting a developing solution onto a support rotating at a certain rate while scanning a developing solution ejection nozzle at a certain rate (dynamic dispense method).

10 [0226]

As the organic solvent contained in the rinse solution used for the rinse treatment after the developing treatment in the solvent developing process, a solvent that is unlikely to dissolve a resist pattern can be appropriately selected from the organic solvents described as the organic solvent used in the organic developing solution and then used. Typically, at least one solvent selected from a hydrocarbon-based solvent, a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, an amide-based solvent, and an ether-based solvent is used. Among these, at least one solvent selected from a hydrocarbon-based solvent, a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, and an amide-based solvent is preferable, at least one solvent selected from an alcohol-based solvent and an ester-based solvent is more preferable, and an alcohol-based solvent is particularly preferable.

These organic solvents may be used alone or in combination of two or more kinds thereof. Further, an organic solvent other than the above-described solvents and water may be mixed and used. Here, in consideration of the development characteristics, the amount of water to be blended into the rinse solution is preferably

25

30% by mass or less, more preferably 10% by mass or less, still more preferably 5% by mass or less, and particularly preferably 3% by mass or less with respect to the total amount of the rinse solution.

A known additive can be blended into the rinse solution as necessary.

- 5 Examples of the additive include a surfactant. As the surfactant, the same surfactants as those described above are exemplary examples. Among these, a non-ionic surfactant is preferable, and a non-ionic fluorine-based surfactant or a non-ionic silicon-based surfactant is more preferable.

- 10 In a case where a surfactant is blended into the solution, the amount of the surfactant to be blended is typically in a range of 0.001% to 5 % by mass, preferably in a range of 0.005% to 2% by mass, and more preferably in a range of 0.01% to 0.5% by mass with respect to the total amount of the rinse solution.

[0227]

- The rinse treatment carried out using a rinse solution (washing treatment) can be performed according to a known rinse method. Examples of the method of performing the rinse treatment include a method of continuously ejecting a rinse solution onto a support rotating at a certain rate (rotary coating method), a method of immersing a support in a rinse solution for a certain time (dip method), and a method of spraying a rinse solution to the surface of a support (spray method).

20 [0228]

- According to the above-described method for forming a resist pattern of the present aspect, since the purified resist composition obtained by the method for producing a purified resist composition according to the first aspect is used, the occurrence of defects during the formation of a resist film is suppressed, and a resist pattern having a satisfactory shape in which defects are reduced can be formed.
- 25

[0229]

(Purified Resist Composition)

The purified resist composition according to a third aspect of the present invention contains a metal compound (M) and an organic solvent component (S). The metal compound (M) contains a metal ion of a metal atom of Group 3 to Group 16 or a metal oxide of the metal atom in the long periodic table, and a bonder that is bonded to the metal ion or the metal oxide. The content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to a total mass of the purified resist composition. The purified resist composition is characterized in that the number of counting 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 1 particle/mL.

[0230]

The purified resist composition according to the present aspect can be obtained by the method for producing a purified resist composition according to the first aspect described above. The purified resist composition obtained by the production 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. As a result, in the purified resist composition according to the present aspect, the number of counting objects having a size of 0.135 μm or more, which are counted by a light scattering-type liquid-borne grain counter, is less than 1 particle/mL, and thus it is possible to realize a purified resist composition having a very small number of foreign substances.

In the purified resist composition according to the present aspect, the number of counting objects having a size of 0.135 μm or more, which are counted by a light scattering-type liquid-borne grain counter, is preferably 0.8 particles/mL or less, more preferably 0.5 particles/mL or less, and still more preferably 0.3 particles/mL or less.

Using the purified resist composition according to the present aspect, it is possible to form a resist pattern having a small number of defects due to a very small number of foreign substances as described above.

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

[0231]

It is preferable that the purified resist composition according to the third aspect has the same composition as the resist composition used in the method for producing a purified resist composition according to the first aspect.

10 [0232]

<<Method for Forming Resist Pattern>>

The method for forming a resist pattern according to a fourth aspect of the present invention includes a step of forming a resist film on a support using the purified resist composition according to the third aspect, a step of exposing the resist film to light,
15 and a step of developing the resist film exposed to light to form a resist pattern.

The method for forming a resist pattern according to the present aspect can be carried out in the same manner as the method for forming a resist pattern according to the second aspect described above.

Examples

20 [0233]

Hereinafter, the present invention will be described in more detail based on examples, but the present invention is not limited to these examples.

[0234]

<Production of Resist Composition>

25 (Production Example 1: Metal Compound (M-1))

0.209 g of monobutyltin oxide hydrate (BuSnOOH) powder (TCI America) was added to 10 mL of 4-methyl-2-pentanol. The resist precursor solution was placed in a closed vial and stirred for 24 hours. The obtained mixture was centrifuged at 4000 rpm for 15 minutes, and insoluble materials were removed by pre-filtration through a 0.45 μ m PTFE syringe, and low-boiling point materials were removed with an evaporator, thereby obtaining a powder of a metal compound (M-1).

[0235]

(Production Example 2: Metal Compound (M-2))

Butyltin diacetate (product code: D0302) was purchased from Tokyo Chemical Industry Co., Ltd., and used as a metal compound (M-2).

[0236]

(Production Example 3: Metal Compound (M-3))

47.0 g of hafnium (IV) ethoxide and 50 g of tetrahydrofuran (THF) were mixed and stirred at 25°C for 10 minutes, mixed with 43.0 g of methacrylic acid, and heated and stirred at 80°C for 5 hours. After completion of the reaction, the mixture was cooled to room temperature and low boiling point substances were removed by an evaporator to obtain a powder of a metal compound (M-3).

[0237]

<Preparation of Resist Composition>

(Resist Compositions 1 to 3)

Each component listed in Table 1 was mixed and dissolved to prepare each resist composition.

[0238]

[Table 1]

	Component (M)	Component (S)
Resist composition 1	(M)-1 [100]	(S)-1 [3000]
Resist composition 2	(M)-2 [100]	(S)-2 [9000]
Resist composition 3	(M)-3 [100]	(S)-3 [3000]

[0239]

In Table 1, each abbreviation has the following meaning. The numerical values in the brackets are blending amounts (parts by mass).

(M)-1 to (M)-3: each of metal compounds (M-1) to (M-3) shown above

5 [0240]

(S)-1: 4-methyl-2-pentanol

(S)-2: n-propanol

(S)-3: PGMEA

[0241]

10 <Production of Purified Resist Composition>

The resist compositions 1 to 3 were each filtered using filters under filtration conditions listed in Table 2 to produce each of the purified resist compositions.

[0242]

[Table 2]

	Resist composition	Filter	Filtration conditions	
			Filtration pressure (MPa)	Filtration temperature (°C)
Example 1	Resist composition 1	1-1	0.2	23
Example 2	Resist composition 2	1-1	0.2	23
Example 3	Resist composition 3	1-1	0.2	23
Example 4	Resist composition 1	1-2	0.2	23
Comparative Example 1	Resist composition 1	2	0.2	23

[0243]

Table 3 lists the filters used for producing the purified resist compositions of each example. The porous membrane in the filters (1) and (1-2) can be obtained according to the production method described in Japanese Unexamined Patent Application, First Publication No. 2017-68262. Further, the average pore diameters of the communication pores of the filters (1-1) and (1-2), obtained by the measurement using a half-dry method (ASTM E1294-89) with a palm porometer (manufactured by PMI), were each about 30 nm and about 50 nm.

[0244]

[Table 3]

Filter	
(1-1)	10-Inch filter that includes porous membrane having porous structure in which communication pores formed by adjacent spherical cells communicating each other are formed Spherical cells having average pore diameter of 100 nm
(1-2)	10-Inch filter that includes porous membrane having porous structure in which communication pores formed by adjacent spherical cells communicating each other are formed Spherical cells having average pore diameter of 300 nm
(2-1)	10-Inch filter including polyethylene porous membrane Filter having pore diameter of 1 nm, manufactured by Entegris, Inc.

[0245]

[Measurement of Content of Metal Atom]

- 5 The content of metal atoms of the purified resist composition of each example before and after filter filtration was measured. The metal compound of each example was heated at 600°C, and the content of the metal compound was determined from the residual mass of the metal oxide. The content of the metal atom with respect to the total mass of the resist composition was calculated from the content of the metal compound.
- 10 The results thereof are listed in the columns of "content of metal atom" in Table 4.

[0246]

[Evaluation of Grain Amount]

- In the purified resist composition of each example, the number of counting objects with a size of 0.135 μm or greater was counted by a dynamic light scattering
- 15 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 rate: 10 mL/min]. The

counting was carried out three times, and the average value thereof was used as the counted value. Further, the light scattering type liquid-borne particle counter was used after calibration with a polystyrene latex (PSL) standard particle solution. The results are listed in the columns of "Particle amount" in Table 4.

5 [0247]

[Evaluation of Coating Defects]

A 12-inch silicon substrate which had been subjected to a hexamethyldisilazane (HMDS) treatment was coated with the purified resist composition of each example using a spinner, and the composition was subjected to a pre-bake (PAB) treatment on a
 10 hot plate at a temperature of 80°C for 60 seconds to dry the composition, thereby forming a resist film having a film thickness of 40 nm. The number of defects larger than 40 nm in the obtained resist film was measured using a surface defect observation device (SurfScan SP5 device, manufactured by KLA-Tencor Corporation). The results thereof are listed in the columns of "number of defects (particles/679 cm²)" in Table 4.

15 [0248]

[Table 4]

	Content of metal atom (%)		Particle amount (particles/mL)	Number of defects (particles/679 cm ²)
Example 1	1.0	1.0	0.3	481
Example 2	0.4	0.4	0.2	289
Example 3	1.7	1.7	0.5	894
Example 4	1.0	1.0	0.5	931
Comparative Example 1	1.0	1.0	1.2	1753

[0249]

As shown in the results listed in Table 4, it was confirmed that the metal concentration in the resist composition was not reduced by filtration. In addition, it was
 20 confirmed that the purified resist compositions of the examples had a reduced amount of particles and coating defects as compared with the purified resist compositions of the

comparative examples.

[0250]

While preferred embodiments 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 invention. Accordingly, the present invention is not limited by the description above but by the scope of the appended claims.

REFERENCE SIGNS LIST

10 [0251]

1a Spherical cell

1b Spherical cell

5 Communication pore

CLAIMS

[Claim 1] A method for producing a purified resist composition, comprising:

a step of filtering a resist composition through a filter having a porous structure in which adjacent spherical cells communicate with each other,

5 wherein the filter includes a porous membrane containing at least one resin selected from the group consisting of polyimide and polyamide-imide,

the resist composition contains a metal compound (M) and an organic solvent component (S),

the metal compound (M) contains a metal ion of a metal atom in Group 3 to
10 Group 16 in a long periodic table or a metal oxide of the metal atom, and a bonder that is bonded to the metal ion or the metal oxide, and

a content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to a total mass of the resist composition.

[Claim 2] The method for producing a purified resist composition according to Claim

15 1,

wherein the metal compound (M) contains at least one selected from the group consisting of tin, indium, antimony, molybdenum, vanadium, tantalum, hafnium, zirconia, iron, and niobium.

[Claim 3] The method for producing a purified resist composition according to Claim 1

20 or 2,

wherein an average pore diameter of the spherical cells is 20 to 2500 nm.

[Claim 4] The method for producing a purified resist composition according to Claim 1 or 2,

wherein an average pore diameter of communication pores formed by the
25 adjacent spherical cells communicating with each other is 1 to 1000 nm, the average pore

diameter being measured by a half-dry method.

[Claim 5] The method for producing a purified resist composition according to Claim 1 or 2,

wherein the filter includes a polyimide porous membrane.

5 [Claim 6] A method for forming a resist pattern, comprising:

a step of obtaining a purified resist composition using the method for producing a purified resist composition according to Claim 1 or 2;

a step of forming a resist film on a support using the purified resist composition;

a step of exposing the resist film to light; and

10 a step of developing the resist film exposed to light to form a resist pattern.

[Claim 7] The method for forming a resist pattern according to Claim 6,

wherein in the step of exposing the resist film to light, the resist film is exposed to extreme ultraviolet rays or electron beams.

[Claim 8] A purified resist composition comprising:

15 a metal compound (M); and

an organic solvent component (S),

wherein the metal compound (M) includes a metal ion of a metal atom in Group 3 to Group 16 in a long periodic table or a metal oxide of the metal atom, and a bonder that is bonded to the metal ion or the metal oxide,

20 a content of the metal atom contained in the metal ion or the metal oxide is 0.2% to 3% by mass with respect to a total mass of the purified resist composition, and

the purified resist composition is formed such that the number of counting objects with a size of 0.135 μm or greater, which is counted by a light scattering type liquid-borne particle counter, is less than 1 particle/mL.

25 [Claim 9] A method for forming a resist pattern comprising:

a step of forming a resist film on a support using the purified resist composition according to Claim 8;

a step of exposing the resist film to light; and

a step of developing the resist film exposed to light to form a resist pattern.

5 [Claim 10] The method for forming a resist pattern according to Claim 9,

wherein in the step of exposing the resist film to light, the resist film is exposed to extreme ultraviolet rays or electron beams.