

[DESCRIPTION]

[Title of Invention]

TOP COAT COMPOSITION, AND METHOD FOR PRODUCING RESIST
PATTERN AND METHOD FOR PRODUCING DEVICE USING SAME

5 [Technical Field]

[0001]

The present invention relates to a top coat composition, a method for
producing a resist pattern and a method for producing a device using the
same.

10 [Background Art]

[0002]

In recent years, the need for higher integration of LSIs has increased,
and finer resist patterns have been required. To meet such a need,
lithography processes using short-wavelength light, such as KrF excimer
15 lasers, ArF excimer lasers, extreme ultraviolet, X-rays, and electron beams,
are becoming more practical.

[0003]

The lithography process for forming fine resist patterns requires high
resolution, but there is a problem in that exposure devices which use short-
20 wavelength light or electron beams are costly. For this reason, immersion
lithography is being considered as a method to solve such problems.

[0004]

Immersion lithography has the advantage that finer resist patterns can be
formed using conventional optics and resist compositions. However, since a
25 resist film is exposed to light while immersing in an immersion liquid such
as water, it is desirable to suppress the elution of resist film components in
the immersion liquid. For this reason, consideration has been given to
forming an additional top coat layer on the formed resist film so as to
achieve more desirable characteristics. It is desirable that such a top coat
30 layer be difficult to dissolve in the immersion liquid, while it is also desirable
that such a top coat layer be easily removed when it comes in contact with
a developer. Therefore, various top coat compositions have been

investigated from this perspective. For example, a top coat composition containing a silicon-containing polymer prepared by hydrolysis and condensation of a silica source, a solvent, optionally a catalyst, and optionally water (PTL 1), an applied aqueous composition containing a plurality of multiple particles applied on a coating layer of a photoresist composition (PTL 2), or a composition that can be used for top coats containing a functionalized polyhedral oligomeric silsesquioxane derivative (PTL 3) has been investigated.

[Citation List]

[Patent Literature]

[0005]

[PTL 1] Japanese Patent Application Publication No. 2007-226244

[PTL 2] Japanese Patent Application Publication No. 2006-337996

[PTL 3] Japanese Patent Application Publication No. 2006-251794

[Summary of Invention]

[Technical Problem]

[0006]

The present inventors have considered as follows. A desirable top coat composition is inert to the immersion liquid and active to the developer, which satisfies contradictory properties.

The present inventors believe that there are still one or more problems which need to be improved in the compounds and compositions for forming cured films. For example, the following problems can be mentioned: high solubility in immersion liquid;

permeability of immersion liquid;

small contact angle to water;

low solubility in developer;

intermixing with a resist film;

high absorption of short wavelength light, and high refractive index;

high required amount of exposure;

low transparency at the exposure wavelength; and

low resolution.

[Solution to Problem]

[0007]

The top coat composition according to the present invention comprises a graft polymer (A) and a solvent (B).

5 The graft polymer (A) comprises a skeleton polymer (AB) moiety and a side chain polymer (AG) moiety, and the side chain polymer (AG) has a cLogP of 15 to 100; and the skeleton polymer (AB) has a cLogP of 1.10 to 3.00.

[0008]

10 The method for producing a resist pattern according to the present invention comprises the following steps:

(1) applying a photosensitive resin composition above a substrate via or not via at least one intermediate layer to form a resist film;

15 (2) applying the top coat composition directly on the resist film to form a top coat;

(3) exposing the top coat and the resist film to radiation; and

(4) developing the top coat and the resist film.

[0009]

20 The method for producing a device according to the present invention comprises the method for producing a resist pattern described above.

[Advantageous Effects of Invention]

[0010]

One or more of the following effects can be expected by using the top coat composition according to the present invention:

25 low solubility in immersion liquid, which suppresses elution of resist film components;

no permeability of immersion liquid;

large contact angle to water;

30 high solubility in developer, which does not affect the steps after the formation of resist patterns;

suppressing intermixing with a resist film;

small absorption of short wavelength light, and low refractive index;

high transparency at the exposure wavelength;
small required amount of exposure ; and
resist patterns with high resolution can be obtained.

[Description of Embodiments]

5 [0011]

[Definition]

In the present specification, the definitions and examples provided in this paragraph are used unless specifically stated otherwise.

10 The singular shall include the plural, and “a” or “the” means “at least one”. An element of a concept can be expressed by a plurality of types, and when an amount (e.g., % by mass or mol%) thereof is described, the amount thereof means a sum of the plurality of types thereof.

“And/or” includes all combinations of elements, and also includes use of either one of the elements.

15 When a numerical range is indicated using “to” or “-”, both end points are included in the range, and the units are common. For example, 5 to 25 mol% means 5 mol% or more and 25 mol% or less.

20 Descriptions such as “C_{x-y}”, “C_x-C_y”, and “C_x” mean the number of carbons in a molecule or a substituent. For example, C₁₋₆ alkyl means an alkyl chain (such as methyl, ethyl, propyl, butyl, pentyl, or hexyl) having from 1 to 6 carbons.

25 When the polymer includes multiple types of repeating units, these repeating units create a copolymer. The copolymer may be any of an alternating copolymer, a random copolymer, a block copolymer, a graft copolymer, or a mixture thereof. When a polymer or a resin is represented by a structural formula, n, m, or the like written in parentheses represents the number of repetitions.

The unit of temperature used is Celsius temperature (degree Celsius). For example, 20 degrees means 20 degrees Celsius.

30 An additive refers to a compound itself that has that function (e.g., a base generator refers to a compound itself that generates a base). There may also be an embodiment in which the compound is dissolved or

dispersed in a solvent and is added to a composition. As an embodiment of the present invention, such a solvent is preferably contained as the solvent (II) or other component in the composition according to the present invention.

5 Aryl refers to a group containing one or more aromatic rings and includes, but is not limited to, phenyl, anthracenyl, naphthyl, phenanthrenyl, fluorenyl, pyrenyl, and the like.

Aralkyl refers to alkyl substituted with aryl and includes, but is not limited to, benzyl, phenylethyl, and the like.

10 [0012]

Hereinafter, embodiments of the present invention will be described in detail.

[0013]

[Top Coat Composition]

15 The top coat composition according to the present invention comprises a graft polymer (A) and a solvent (B). This top coat composition can be used in the same manner as conventionally known top coat compositions. This top coat composition will be described below.

[0014]

20 (A) Graft Polymer

The graft polymer used in the present invention comprises a skeleton polymer (AB) moiety and a side chain polymer (AG) moiety. The skeleton polymer (AB) moiety and the side chain polymer (AG) moiety each have cLogP within specific ranges. Specifically, the cLogP of the side chain polymer (AG) is 15 to 100, and the cLogP of the skeleton polymer (AB) is 1.10 to 3.00. In other words, the graft polymer (A) used in the present invention has a highly hydrophobic side chain polymer (AG) moiety and a relatively less hydrophobic (preferably hydrophilic) skeleton polymer (AB) moiety.

25 30 [0015]

The ratio of (the cLogP of the side chain polymer (AG))/(the cLogP of the skeleton polymer (AB)) is preferably 5 to 30. By satisfying this condition, the

hydrophobic/hydrophilic difference between the side chain polymer (AG) moiety and the skeleton polymer (AB) moiety becomes noticeable, and the effect of the present invention is even more noticeable.

[0016]

5 Furthermore, the graft polymer (A) preferably has a cLogP of 3 to 9.5.

[0017]

In the present invention, cLogP is the value for calculating the ordinary logarithm LogP of the partition coefficient P in 1-octanol and water. A cLogP can be calculated by the method described in "Prediction of Hydrophobic (Lipophilic) Properties of Small Organic Molecules" (Arup K. Ghose et al., J. Phys. Chem. A, 1998, 102, 3762-3772). In the present description, the cLogP of the graft polymer (A) with graft chains is calculated using ChemAxon MarvinSketch Helium.2 by calculating the cLogP of each repeating unit and adding the cLogP × composition ratio of each repeating unit.

15

[0018]

The cLogP of the side chain polymer (AG) is calculated using all the repeating units and the repeating numbers calculated from the number average molecular weight. The cLogP of the skeleton polymer (AB) is calculated using each repeating unit and the composition ratio thereof after excluding the repeating units of the side chain polymer (AG) from the graft polymer (A).

20

[0019]

The cLogP of the graft polymer (A) is calculated using the repeating units including the repeating units of the side chain polymer (AG) and the composition ratio thereof.

25

[0020]

When calculating a cLogP for each repeating unit, the calculation is made under the assumption that polymerization has occurred for each repeating unit, and terminals outside the repeating units are not included.

30

[0021]

For example, when the skeleton polymer (AB) moiety of the graft polymer (A) is constituted of three repeating units a, b, and c, the cLogP thereof are 0.48, 0.35, and 1.02, respectively, the composition ratio is 6:2:1, the cLogP of the side chain polymer (AG) is 10, and the composition ratio is 1, the cLogP of the graft polymer (A) is 1.46, and the cLogP of the skeleton polymer (AB) is 0.51.

[0022]

In the graft polymer (A) used in the present invention, the number average molecular weight (Mn) of the side chain polymer (AG) moiety is preferably 4,000 to 35,000 and more preferably 4,000 to 20,000.

[0023]

The mass average molecular weight (Mw) of the graft polymer (A) is preferably 6,000 to 100,000 and more preferably 8,000 to 30,000. The Mw of the side chain polymer (AG) moiety constituting the graft polymer (A) is preferably 5,000 to 30,000, and the Mw of the skeleton polymer (AB) moiety is 6,000 to 30,000. The mass average molecular weight herein is a mass average molecular weight in terms of polystyrene and can be measured by gel permeation chromatography based on polystyrene.

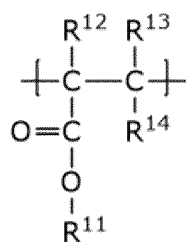
[0024]

The graft polymer (A) is specified by the cLogP of the skeleton polymer (AB) moiety and the cLogP of the side chain polymer (AG) moiety, as described above, and the chemical composition is not limited as long as the above feature is satisfied. However, the following is preferable as the chemical composition.

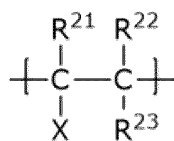
[0025]

It is preferable that the graft polymer (A) comprise at least one repeating unit represented by formula (a-1) or (a-2):

[C1]



(a-1)



(a-2)

wherein

R¹¹ represents hydrogen or a linear, branched, or cyclic C₁₋₃₀ hydrocarbon group, where the hydrocarbon group can be substituted with hydroxy or carboxy;

R¹² to R¹⁴ and R²¹ to R²³ each independently represent hydrogen or a linear, branched, or cyclic C₁₋₃₀ hydrocarbon group;

the hydrocarbon group each can be substituted with fluorine, hydroxy, or alkoxy; and

any -CH₂- in the hydrocarbon group can be substituted with -O- or -CO-, where the -CH₂- (methylene group) includes terminal methyl; and

X is the side chain polymer (AG) moiety and is a polymer moiety comprising at least one siloxane bond.

[0026]

R¹¹ to R¹⁴, R²¹ to R²³, and X may configure the side chain polymer (AG) moiety of a graft polymer. For example, if any of R¹¹ to R¹⁴ and R²¹ to R²³ is a hydrocarbon group having larger carbon numbers and does not include a highly hydrophilic substituent, such as hydroxy, cLogP can be 15 or more.

X in formula (a-2) is a substituent comprising a siloxane bond, and a siloxane bond increases cLogP. Thus, for example, the cLogP of a group comprising a polysiloxane structure can be 15 or more.

[0027]

Meanwhile, for example, when any of R¹¹ to R¹⁴ in formula (a-1) have smaller carbon numbers or comprise a highly hydrophilic substituent, cLogP tends to be lower. If the number of siloxane bonds included in X in formula (a-2) is small, cLogP may also be low. When such a repeating unit that

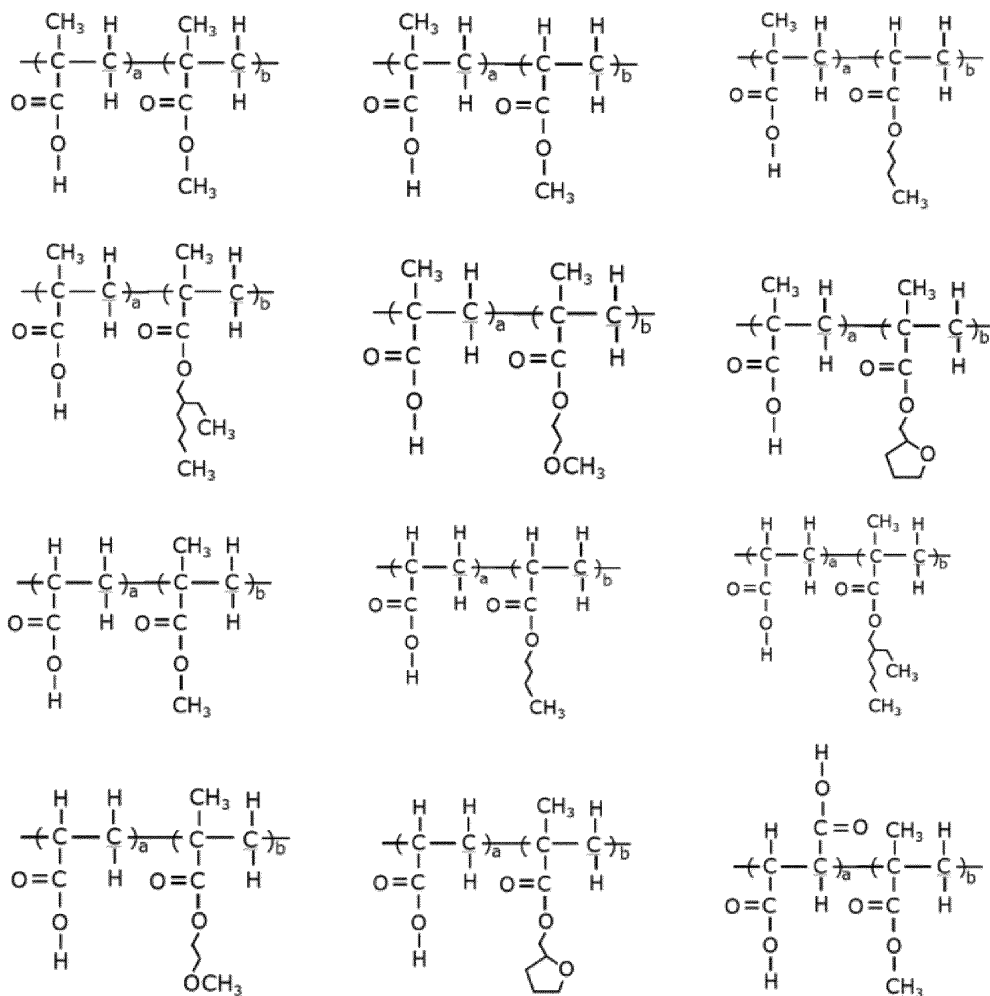
reduces cLogP is bonded, the cLogP of the skeleton polymer (AB) may be low and may be within the range of 1.10 to 3.00.

[0028]

Specific examples of formula (a-1) include the following:

5

[C2-1]

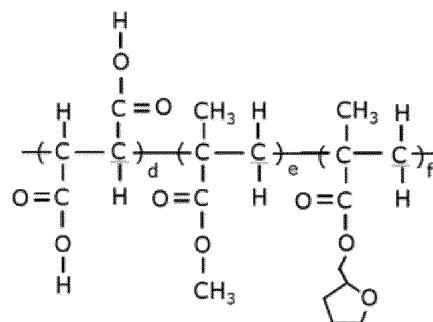
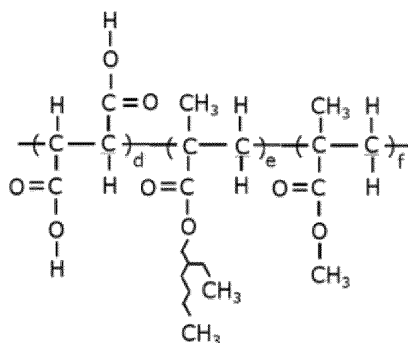
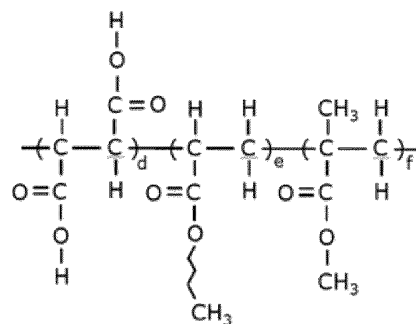
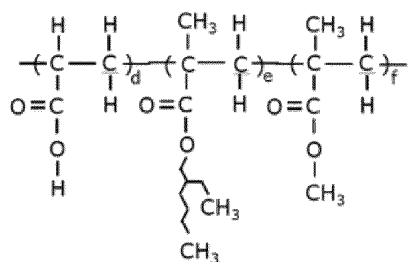
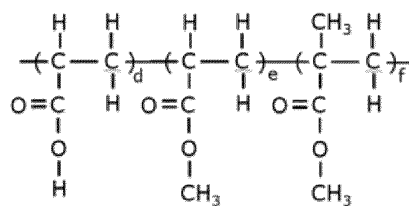
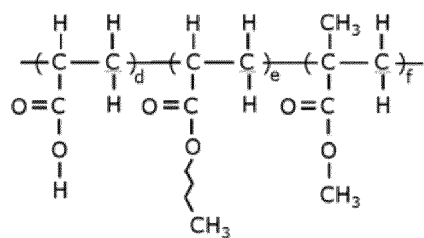


[0029]

[C2-2]

wherein

each repeating unit may be randomly bonded or form blocks;



[0033]

wherein

each repeating unit may be randomly bonded or form blocks;

5

d, e, and f are proportions (%) of repeating units and are each

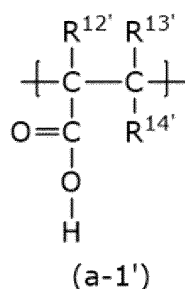
independently the number larger than 0, provided that $d + e + f = 100$.

[0034]

For example, it is preferable that the skeleton polymer (AB) moiety be a polymer comprising at least one repeating unit represented by formula (a-1'):

10

[C4]



wherein

R^{12'} to R^{14'} each independently represent hydrogen, -COOH, or a linear, branched, or cyclic C₁₋₃₀ hydrocarbon group;

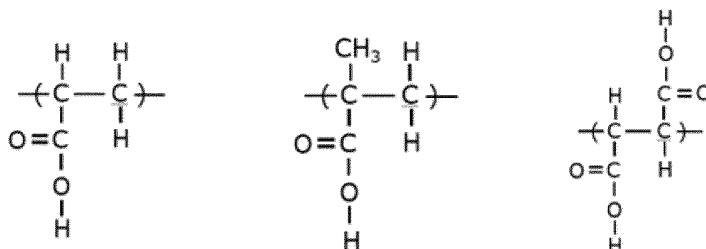
5 the hydrocarbon group each can be substituted with fluorine, hydroxy, or alkoxy; and

any -CH₂- in the hydrocarbon group can be substituted with -O- or -CO-, where the -CH₂- (methylene group) includes terminal methyl.

[0035]

10 The following are specific examples of repeating units represented by formula (a-1').

[C5]



[0036]

15 Such repeating units are produced by polymerizing acrylic acid, methacrylic acid, or esters thereof. Specifically, it is preferable that the skeleton polymer (AB) moiety be a polymer of at least one monomer selected from the group consisting of methacrylic acid, acrylic acid, butyl acrylate, methyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, β-carboxyethyl (meth)acrylate, maleic acid, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, a ring-opened product of

20

glycidyl (meth)acrylate, methoxyethyl (meth)acrylate, polyalkoxyalkyl (meth)acrylate, and tetrahydrofurfuryl (meth)acrylate.

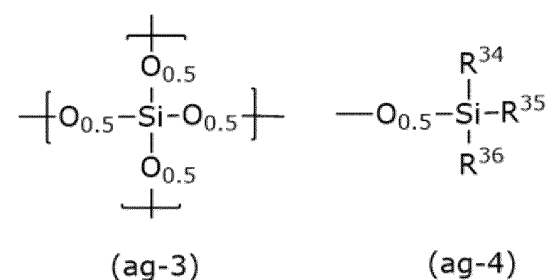
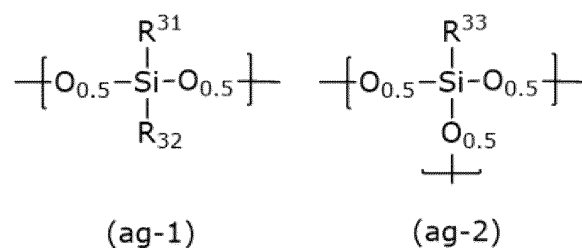
[0037]

5 Such a skeleton polymer (AB) is preferably a linear polymer. A skeleton polymer (AB) constituted by the monomers described above is a linear polymer.

[0038]

10 It is typically preferable that the side chain polymer (AG) moiety, which is a relatively highly hydrophobic portion, comprise a polysiloxane structure. In this case, it is preferable that the side chain polymer (AG) moiety comprising a polysiloxane structure be a polymer comprising at least one repeating unit represented by formula (ag-1), (ag-2), or (ag-3) and a terminal group represented by formula (ag-4):

[C6]



15

wherein

R³¹ to R³⁶ each independently represent hydrogen, a linear, branched, or cyclic C₁₋₃₀ saturated aliphatic hydrocarbon group, or a C₆₋₃₀ aromatic hydrocarbon group;

the aliphatic hydrocarbon group and the aromatic hydrocarbon group can each be substituted with fluorine or alkoxy; and any -CH₂- in the aliphatic hydrocarbon group and the aromatic hydrocarbon group can be substituted with -O- or -NH-, where the -CH₂- (methylene group) includes terminal methyl.

[0039]

A polysiloxane structure can contain silanol. This silanol refers to a functional group in which an OH group is bonded directly to the Si skeleton of polysiloxane. The silanol content varies, depending on the synthetic condition of polysiloxane, such as the monomer mixing ratio or the type of reaction catalyst. The silanol content can be evaluated by quantitative infrared absorption spectrum measurement. The absorption band attributed to silanol (SiOH) appears as an absorption band having a peak of $900 \pm 100 \text{ cm}^{-1}$ in the infrared absorption spectrum. When the silanol content is high, the intensity of this absorption band is high.

[0040]

When the polysiloxane of the side chain polymer (AG) used in the present invention is measured and analyzed by the FT-IR method, the ratio S2/S1 between the area intensity S1 of the absorption band attributed to Si-O in the range of $1100 \pm 100 \text{ cm}^{-1}$ and the area intensity S2 attributed to SiOH in the range of $900 \pm 100 \text{ cm}^{-1}$ is 0.00 to 0.050, preferably 0.00 to 0.020. In a preferred embodiment, the side chain polymer (AG) does not contain silanol (S2/S1 = 0.00).

[0041]

The area intensity of the absorption band is determined to account for noises of the infrared absorbing spectrum or the like. In a typical infrared absorbing spectrum of polysiloxane, an absorption band attributed to Si-OH having a peak within the range of $900 \pm 100 \text{ cm}^{-1}$ and an absorption band attributed to Si-O having a peak within the range of $1100 \pm 100 \text{ cm}^{-1}$ are observed. The area intensity of these absorption bands can be measured as an area based on the baseline to account for noises or the like. There may be cases where the tails of the absorption bands attributed to Si-OH

and Si-O overlap. In such cases, the wavenumber corresponding to the minimum point between the two absorption bands in the spectrum is used as the boundary. The same is true for the case where the tails of other absorption bands overlap with the tails of the absorption band attributed to Si-OH or Si-O.

[0042]

The mixing ratio of (ag-1) to (ag-3) is not particularly limited. However, when (ag-2) and (ag-3) are included, it is possible to incorporate a branched structure. But variations in molecular weight easily occur during the manufacturing process, which may affect the stability of the performance of the top coat composition. Typically, polysiloxane structures with a high proportion of linear portions are easy to use, and those with a high proportion of (ag-1) are preferably used. Specifically, the ratio of the number of repeating units (ag-1) to the total number of repeating units (ag-1) to (ag-3) is preferably 90% or more. Linear polysiloxane structures or polysiloxane structures having one branched structure are typically used.

[0043]

The side chain polymer (AG) moiety having a structure composed of such repeating units may constitute X in formula (a-2).

[0044]

The side chain polymer (AG) moiety described above can be directly bonded to the skeleton polymer (AB) moiety and can also be bonded via a linking group. For example, the side chain polymer (AG) moiety described above can be bonded to the skeleton polymer (AB) moiety via a linking group represented by formula (x-1).

*-D-E-F-G-# (x-1)

wherein

* denotes a site to be linked to the skeleton polymer (AB) moiety,

denotes a site to be linked to the side chain polymer (AG) moiety,

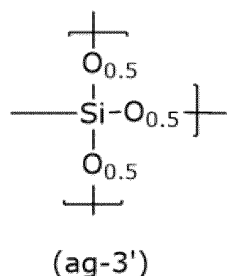
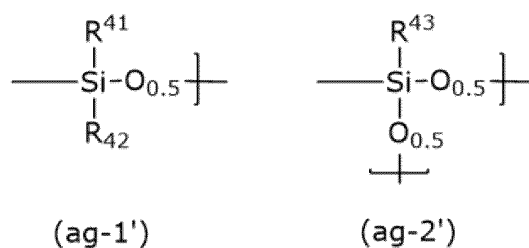
D is a single bond or -CO-,

E is a single bond, -O-, -NH-, or -S-,

F is a single bond or a divalent C₁₋₁₂ hydrocarbon group in which -CH₂- can be substituted with -O- or -NH-, and

G is represented by one of formula (ag-1'), (ag-2'), or (ag-3'):

[C7]



5

wherein

R⁴¹ to R⁴³ each independently represent hydrogen, a linear, branched, or cyclic C₁₋₃₀ saturated aliphatic hydrocarbon group, or a C₆₋₃₀ aromatic hydrocarbon group;

10

the aliphatic hydrocarbon group and the aromatic hydrocarbon group can each be substituted with fluorine or alkoxy; and

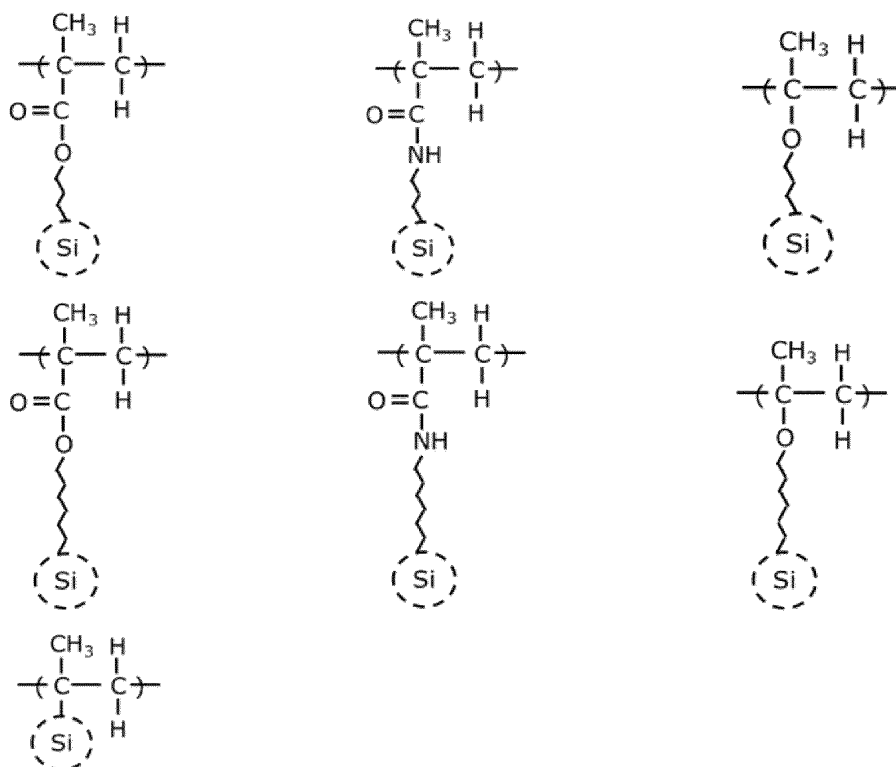
any -CH₂- in the aliphatic hydrocarbon group and the aromatic hydrocarbon group can be substituted with -O- or -NH-, where the -CH₂- (methylene group) includes terminal methyl.

15

[0045]

The following are specific examples of repeating units represented by formula (a-2):

[C8]



[0046]

wherein

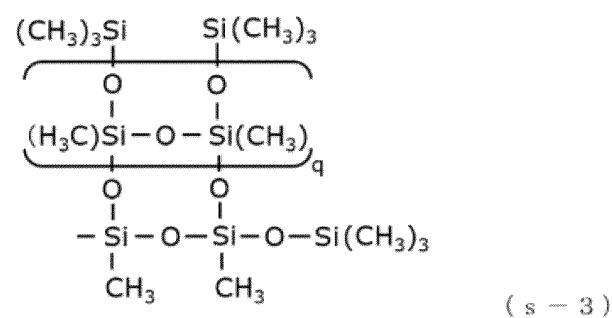
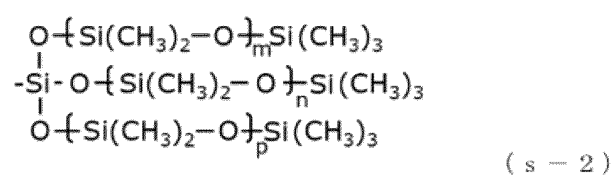
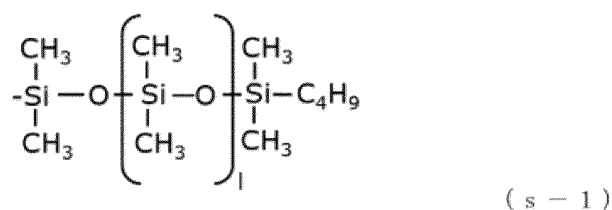
[C9]



5

is a polysiloxane moiety of the side chain polymer (AG) and represented by formulas (s-1) to (s-3);

[C10]



wherein

l, m, n, p, and q are each independently an integer of 1 or more.

[0047]

- 5 The graft polymer (A) used in the present invention comprises the skeleton polymer (AB) moiety and the side chain polymer (AG) moiety, and the mass ratio thereof is not limited. However, from the viewpoint of maintaining high solubility of graft polymer (A), the mass ratio (AG/A) of the side chain polymer (AG) moiety based on the total mass of graft polymer
- 10 (A) is preferably 10.0% to 50.0% by mass, more preferably 12.0% to 30.0% by mass.

[0048]

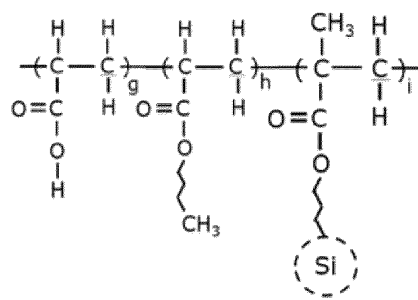
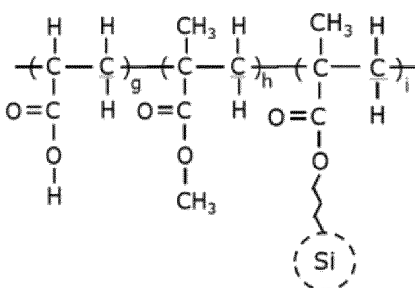
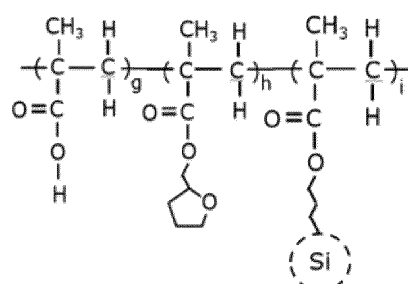
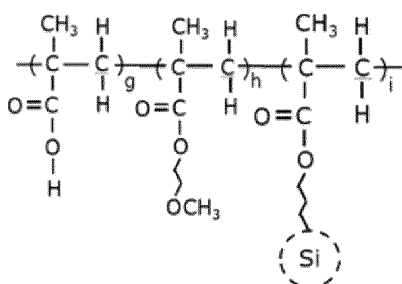
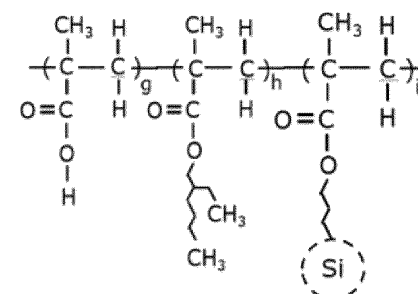
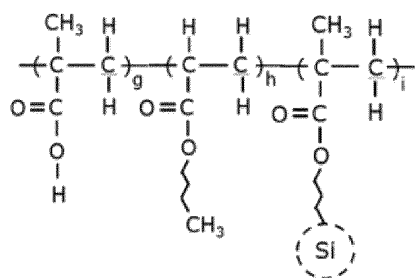
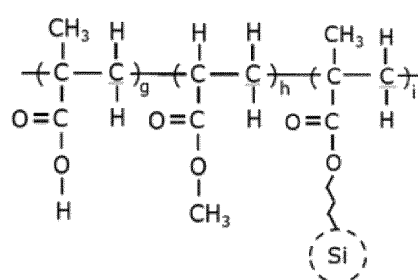
- 15 The production method of the graft polymer (A) that can be used in the present invention is not particularly limited. For example, a compound that can form a repeating unit as represented by formula (a-1) and does not

5 have a side chain polymer (AG) moiety and, for example, a compound that can form a repeating unit as represented by formula (a-2) and has an X moiety corresponding to the side chain polymer (AG) moiety. Alternatively, a side chain polymer (AG) moiety with a cLogP of 15 to 100 may be coupled as a side chain with a skeleton polymer (AB) moiety with a cLogP of 1.10 to 3.00.

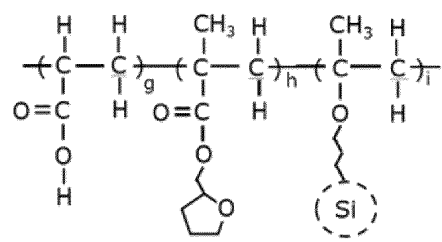
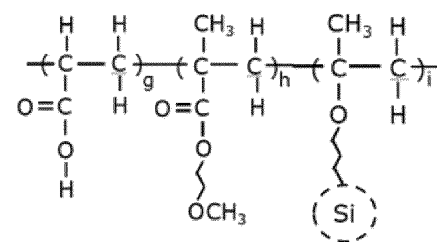
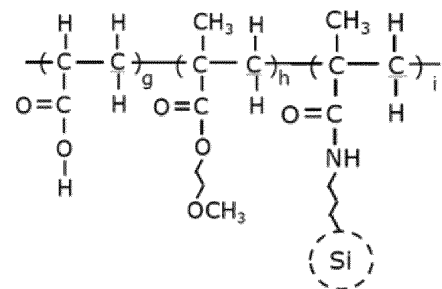
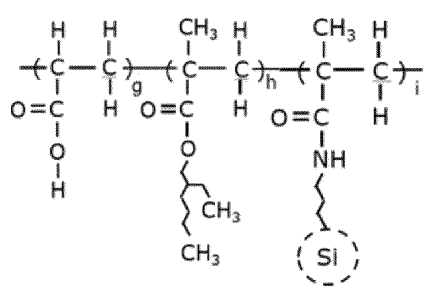
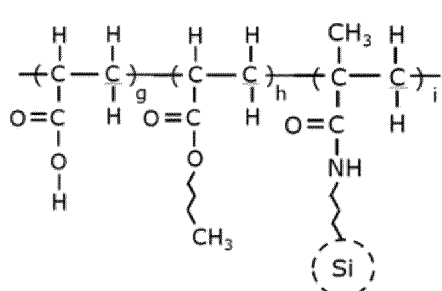
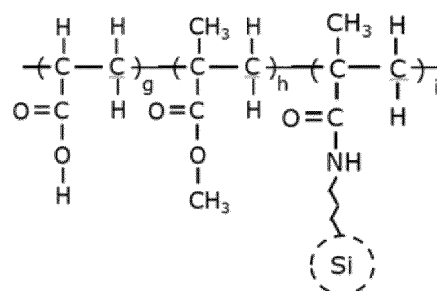
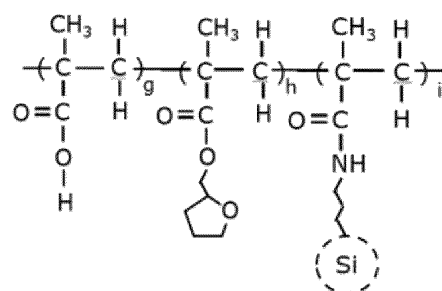
[0049]

Specific examples of graft polymers (A) include the following:

[C11-1]



[C11-2]



[C11-4]

wherein

g, h, and i are proportions (%) of repeating units and each independently the number larger than 0, provided that $g + h + i = 100$; and

[C12]

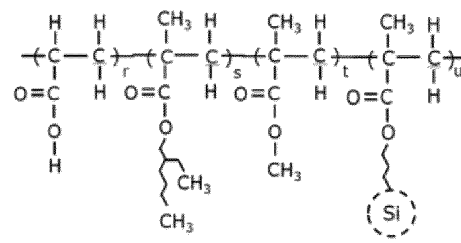


5

is as defined above;

[0057]

[C13]



r, s, t, and u are proportions (%) of repeating units and each independently the number larger than 0, provided that $r + s + t + u = 100$; and

[C14]



is as defined above.

[0059]

(B) Solvent

5 The top coat composition according to the present invention further comprises a solvent (B). Solvents are not particularly limited as long as the solvent can dissolve the graft polymer (A) described above. Such solvents include water (B1) and organic solvents. Water-soluble organic solvents are preferred as organic solvents, and examples thereof include alcohol
10 solvents (B2), ketone solvents, amide solvents, glycol ether solvents, ester solvents, and the like. Among these solvents, water is preferably used. Mixed solvents of water and water-soluble organic solvents can also be used, but the content ratio of water-soluble organic solvents is preferably 50.0% by mass or less, and more preferably 20.0% by mass or less. For
15 example, the content of the alcohol solvent (B2) is 0% to 5.0% by mass based on the total mass of solvent (B). When a water-soluble organic solvent is used, it is preferable to use an alcohol solvent (B2). As alcohol solvents, relatively lower alcohols such as methanol, ethanol, isopropanol, and methoxyethanol are preferable. Most typically, the top coat composition
20 according to the present invention does not contain an organic solvent. In an embodiment, the content of the solvent (B) is 75% to 99.5% by mass based on the total mass of the top coat composition. In an embodiment, the content of the water (B1) is 80% to 99.99% by mass based on the total mass of the solvent (B). In an embodiment, the content of the graft polymer
25 (A) is 0.5% to 5% by mass based on the total mass of the top coat composition.

[0060]

(C) Surfactant

In the top coat composition according to the present invention, which comprises the graft polymer (A) and the solvent (B) described above as essential components, other components may be contained as needed.
[0061]

5 One such component is a surfactant. A surfactant can improve the coatability of the top coat composition when the top coat composition is applied on the resist film. Surfactants include cationic surfactants, anionic surfactants, and nonionic surfactants, and any of these can be selected and used according to the purpose. When used, the content of the surfactant is
10 preferably 0% to 5% by mass and more preferably 0.05% to 1% by mass based on the total mass of the top coat composition. An embodiment in which the composition of the present invention does not contain the component (C) is also a preferred embodiment of the present invention.
[0062]

15 (D) Base

 The top coat composition according to the present invention may comprise a base (D) as needed. The base (D) can adjust the pH of the top coat composition or improve the solubility of the formed top coat in a developer, or the like. When used, the content of the base is preferably 0%
20 to 5% by mass and more preferably 0.05% to 1% by mass based on the total mass of the top coat composition. An embodiment in which the composition of the present invention does not contain the component (D) is also a preferred embodiment of the present invention.
[0063]

25 (E) Other Additives

 The top coat composition according to the present invention may further comprise other additives (E). Other additives herein are preferably at least one selected from the group consisting of an acid, a lower alcohol (C₁₋₆ alcohol), a surface leveling agent, an adhesion agent, a defoamer, and a
30 preservative. The content of other additives is adjusted according to the purpose. When used, the content of other additives is preferably 0% to 5% by mass and more preferably 0.05% to 1% by mass based on the total

mass of the top coat composition. An embodiment in which the composition of the present invention does not contain the component (E) is also a preferred embodiment of the present invention.

[0064]

5 The top coat composition according to the present invention comprises each component described above and is normally in the form of a solution, not a suspension. Particularly, the graft polymer (A) is dissolved in the top coat composition and does not exist in the form of colloidal particles.

[0065]

10 A preferable top coat composition according to the present invention has high stability and causes almost no change in physical properties even if the top coat composition is stored at room temperature. For example, it is preferable that the top coat composition do not gel even after standing still at room temperature for 12 hours. It is preferable that the top coat
15 composition have a viscosity of 1 to 100 mPa·s after standing at room temperature for 12 hours. The viscosity can be measured using a Cannon-Fenske viscometer at 25°C.

[0066]

20 The top coat composition according to the present invention can be used similarly to a top coat composition normally used in immersion lithography. This top coat composition can be a liquid immersion top coat composition that is applied directly on a formed liquid immersion resist film or, if necessary, above a resist film via an intermediate film, and more specifically, can be a liquid immersion resist upper layer film composition.
25 This top coat composition is particularly preferably used in immersion lithography exposed to light with a short wavelength and is preferably a liquid immersion ArF resist upper layer film composition using ArF laser as an exposure light source. In another embodiment, the top coat composition is a liquid immersion top anti-reflective coating composition for ArF resists.

30 [0067]

 The top coat composition according to the present invention is applied directly on the resist film and then cured by drying to form a top coat, as

described below. This top coat is preferably less soluble in an immersion liquid used for immersion lithography, for example, water, and it is more preferable that the top coat do not dissolve in water. While not bound by any theory, it is believed that since the skeleton polymer (AB) is hydrophilic, the graft polymer (A) is water-soluble and can suppress component elution from the resist film and intermixing. And since the side chain polymer (AG) is hydrophobic, the top coat does not dissolve in water, and component elution from the resist film during an immersion lithography step can be suppressed.

[0068]

It is preferable that a top coat formed from the top coat composition according to the present invention can be easily removed when developed after the immersion lithography of the resist film. Specifically, the top coat is preferably highly soluble in an alkaline developer, for example, a 2.38% aqueous tetramethylammonium hydroxide solution.

[0069]

It is preferable that a top coat formed from the top coat composition according to the present invention by applying the top coat composition on a resist film and the resist film do not intermix at the interface therebetween. With suppressed intermixing at the interface, the smoothness of the interface is less likely to be impaired, and the resist film is less likely to be affected by components contained in the top coat composition.

[0070]

The top coat formed from the top coat composition according to the present invention preferably has a low refractive index. A low refractive index of the top coat can suppress the reflection inside the resist film and high resolution can be maintained. In the present invention, the refractive index n of the top coat with respect to the light of ArF laser with a wavelength of 193 nm, which is typically used in immersion lithography, is preferably 1.40 to 1.80. In the present invention, the extinction coefficient k of the top coat with respect to the light with a wavelength of 193 nm is preferably 0.00 to 0.25.

[0071]

[Production Method of Resist Pattern]

The top coat composition according to the present invention can be used in the manufacture of a resist pattern. The resist pattern production method according to the present invention comprises the following steps, for example:

- (1) applying a photosensitive resin composition above a substrate with or without one or more intermediate layers to form a resist film;
- (2) applying any one of the top coat compositions described above directly on the resist film to form a top coat;
- (3) exposing the top coat and the resist film to radiation; and
- (4) developing the top coat and the resist film.

[0072]

A resist film is formed above a substrate. The resist film can be formed by any method among commonly known methods.

[0073]

As a substrate, a silicon/silicon dioxide-coated substrate, a silicon nitride substrate, a silicon wafer substrate, a glass substrate, an ITO substrate, or the like can be used.

[0074]

In the present invention, the term of above includes a case of being formed directly on and a case of being formed with another layer interposed. For example, a planarization film or a bottom anti-reflective coating can be formed directly on a substrate, and a photosensitive resin composition can be applied directly thereon. A preferred embodiment of the present invention includes applying a photosensitive resin composition directly on a substrate to form a resist film. Application methods are not particularly limited, but include, for example, an application with spin coaters, slit coaters, and other methods.

[0075]

Photosensitive resins included in the photosensitive resin composition are not particularly limited and a photosensitive resin suitable for the

purpose can be selected. In the method for producing a resist pattern in the present invention, since it is particularly desirable to form a pattern with high resolution, a lithography process using light with a short wavelength is employed. Thus, a photosensitive resin with high sensitivity to the light used
5 is selected. The photosensitive resin with high sensitivity to the light of KrF and ArF are preferable. The photosensitive resin with high sensitivity to the light of ArF is more preferable. Compositions with higher sensitivity are preferred, and it is preferable that the photosensitive resin composition be a chemically amplified photosensitive resin composition.

10 [0076]

A photosensitive resin composition is applied to a substrate and thereafter preferably heated to form a resist film. The heating temperature in this case is preferably 75°C to 140°C, more preferably 80°C to 130°C, and further preferably 90°C to 120°C. The heating time is preferably 30 to
15 240 seconds and more preferably 90 to 180 seconds. Heating is preferably performed under air or nitrogen gas atmosphere. The film thickness of the resist film is preferably 50 to 1,000 nm, more preferably 80 to 800 nm, and further preferably 100 to 600 nm. It is noted that heating can be performed after applying the top coat composition described below.

20 [0077]

Subsequently, any one of the top coat compositions described above is applied directly on the resist film to form a top coat. The application method of the top coat composition is not particularly limited, and, for example, an application with spin coaters, slit coaters, and other methods can be used.

25 [0078]

After the application of the top coat composition, heating is performed as needed. This heating can be performed simultaneously with the heating of the photosensitive resin composition described above. In order to simplify the process, it is preferable to preheat the photosensitive resin composition
30 at a relatively low temperature after application of the photosensitive resin composition to dry the photosensitive resin composition. And then the top

coat composition is applied, followed by the above heating to form the resist film and the top coat.

[0079]

5 After the formation of the top coat, the top coat and the resist film are exposed to radiation. Light sources of radiation for exposure and exposure methods are not particularly limited. In order to achieve higher resolution, it is preferable to use radiation with short wavelengths, such as ArF or KrF, especially ArF, and is preferable to employ immersion lithography as the exposure method. In immersion lithography, a top coat and a
10 photosensitive resin layer are immersed in an immersion liquid, for example, water, and then subjected to exposure in the immersion liquid. The resist film is generally exposed through a mask.

[0080]

The exposed top coat and resist film are heated as needed after the
15 exposure. The temperature of heating after the exposure is preferably 100°C to 200°C and more preferably 150°C to 190°C, and the heating time is preferably 30 to 240 seconds and more preferably 90 to 180 seconds. The exposed resist film is developed using a developer to form a resist pattern. Alkali development and organic solvent development can be used
20 as the development. Alkali development, particularly development with a 2.38% aqueous tetramethylammonium hydroxide solution, is preferred.

[0081]

If necessary, the developed top coat and photosensitive resin layer can
25 be washed with a rinse solution to provide a resist pattern with high resolution.

[0082]

[Production Method of Device]

The production method of a device according to the present invention
30 comprises any one of the methods for producing a resist pattern described above. The method for producing a resist pattern described above can form a resist pattern with high resolution. A device with a higher degree of integration can be manufactured due to the high resolution of the resist

pattern when the method for producing a device according to the present invention is employed.

[0083]

5 In more detail, it is preferred to further comprise a step of etching a resist pattern produced by any one of the methods for producing a resist pattern according to the present invention described above as a mask to process a substrate. This method enables processing for forming wiring grooves and the like on the substrate to be performed. By forming wiring on the processed substrate, it is possible to manufacture devices with a high
10 degree of integration.

[0084]

The present invention will be further described in more detail below with Examples and Comparative Examples, but the present invention is not limited to these Examples and Comparative Examples.

15 [0085]

In the following examples, a mass average molecular weight (Mw) is measured by gel permeation chromatography (GPC) using polystyrene as a standard. GPC is performed using Alliance™ e2695 high-speed GPC system (Nihon Waters K.K.) and an organic solvent GPC column Shodex
20 KF-805L (Showa Denko K.K.). The measurement is performed using monodisperse polystyrene as the reference sample and chloroform as the eluent at a flow rate of 0.6 mL/min and a column temperature of 40°C. Mw is then calculated as the molecular weight relative to the reference sample.

[0086]

25 The S2/S1 ratio of the side chain polymers (AG) is measured using a solution cell. FT-IR spectra are measured at room temperature using FTIR-6100 (JASCO Corporation). The baseline is corrected to account for noise, and the area intensities of the absorption band (S2) attributed to Si-OH with a peak in the range of $900 \pm 100 \text{ cm}^{-1}$ and the absorption band (S1) attributed to Si-O with a peak in the range of $1100 \pm 100 \text{ cm}^{-1}$ are
30 measured, and the value of S2/S1 is calculated. There may be cases where the tails of the absorption bands attributed to Si-OH and Si-O overlap. In

such cases, the wavenumber corresponding to the minimum point between the two absorption bands in the spectrum is used as the boundary. The same is true for the case where the tails of other absorption bands overlap with the tails of the absorption band attributed to Si-OH or Si-O.

5 [0087]

[Synthetic Example A1 of Graft Polymer (A)]

First, 30 parts by mass of FM-0721 (methacrylic monomer JNC having a polydimethylsiloxane structure with a number average molecular weight of 5,000) as a side chain polymer (AG), 50 parts by mass of methyl
10 methacrylate (Tokyo Chemical Industry Co., Ltd.), and 20 parts by mass of methacrylic acid (FUJIFILM Wako Pure Chemical Corporation), as monomers for forming a skeleton polymer (AB), 1 part by mass of 3-mercaptopropionic acid (Tokyo Chemical Industry Co., Ltd.) as a chain transfer agent, and 100 parts by mass of isopropanol as a solvent are fed in
15 a separable flask equipped with a reflux condenser, a thermometer, a stirrer, and a constant temperature reaction device. Oxygen in the fed materials is purged by nitrogen bubbling to replace the atmosphere in the separable flask with nitrogen. While stirring the fed materials, 1 part by mass of 2,2'-azobis(isobutyronitrile) (AIBN: FUJIFILM Wako Pure Chemical
20 Corporation) is fed and reacted at 80°C for 4 hours. Then, 0.5 parts by mass of AIBN is further fed and reacted at the same temperature for 4 hours. To the resulting solution, 200 parts by mass of a solution of 17.4 parts by mass of dimethylaminoethanol in deionized water are gradually added under stirring. Isopropanol is distilled off under a reduced pressure
25 condition at 50°C, and deionized water (B1) is added for solid content adjustment to obtain an aqueous solution of graft polymer (A1) with a solid content of 25%.

The S2/S1 ratio of FM-0721 is 0.00.

[0088]

30 [Synthetic Examples A2 to A7 of Graft Polymer (A)]

Graft polymers (A) of synthetic examples A2 to A7 are synthesized such that the component and content be those listed in the following Table 1-1.

The S2/S1 ratios of FM-0725 and FM-0711 are both 0.00. Table 1-2 shows the cLogP and Mw of each polymer.

[0089]

[Table 1-1]

Table 1-1

Graft polymer (A)	Side chain polymer (AG)			MA	AA	MMA	BAA	EHMA	MPA	AIBN	DMAE
	AG1	AG2	AG3								
A1	30	-	-	20	-	50	-	-	1	1.5	17.4
A2	-	30	-	20	-	50	-	-	1	1.5	17.4
A3	13	-	-	20	-	67	-	-	1	1.5	17.4
A4	30	-	-	20	-	-	50	-	1	1.5	17.4
A5	30	-	-	20	-	-	-	50	1	1.5	17.4
A6	-	-	30	20	-	50	-	-	1	1.5	17.4
A7	30	-	-	-	30	40	-	-	1	1.5	17.4

In the table,

AG1: FM-0721 (Mn 5,000)

AG2: FM-0725 (Mn 10,000)

AG3: FM-0711 (Mn 1,000)

MA: Methacrylic acid

AA: Acrylic acid

MMA: Methyl methacrylate

BAA: Butyl acrylate

EHMA: 2-Ethylhexyl methacrylate

MPA: 3-Mercaptopropionic acid

AIBN: 2,2'-Azobis(isobutyronitrile)

DMAE: Dimethylaminoethanol

[Table 1-2]

Table 1-2

Graft polymer (A)	cLogP			(AG)cLogP /(AB)cLogP	Mw
	AG	AB	A		
A1	15.46	1.13	5.43	13.7	16,500
A2	28.10	1.13	9.22	24.9	18,800
A3	15.46	1.14	3.00	13.6	17,200
A4	15.46	1.68	5.82	9.2	16,000
A5	15.46	3.28	6.94	4.7	15,800
A6	5.30	1.13	2.38	4.7	12,500
A7	15.46	0.87	5.25	17.7	15,400

[0090]

[Preparation Examples of Examples 1 to 6 and Comparative Examples 1 to 3]

5 The compositions of each example are prepared to have the components and contents listed in Table 2, stirred at room temperature for 30 minutes, and filtered (pore size = 10 nm) to obtain the top coat composition. The graft polymer (A) is used in a 25% by mass aqueous solution obtained in the synthetic examples, and the content in the table is

10 the content of the graft polymer.

[0091]

[Table 2]

Table 2

	Graft polymer (A)		Water	ME	S
Example 1	A 1	2	The remainder	-	-
Example 2	A 1	2	The remainder	-	0.14
Example 3	A 1	2	The remainder	17	-
Example 4	A 2	2	The remainder	-	-
Example 5	A 3	2	The remainder	-	-
Example 6	A 4	2	The remainder	-	-
Compar. Ex. 1	A 5	2	The remainder	-	-
Compar. Ex. 2	A 6	2	The remainder	-	-
Compar. Ex. 3	A 7	2	The remainder	-	-

In the table,

ME: Methoxyethanol

S: Surfactant, TAKESURF A-32-FW (Takemoto Oil & Fats Co., Ltd.)

[0092]

5 [Evaluation]

For the composition for each example obtained, the homogeneity of the top coat composition, the solubility of the formed top coat in deionized water, the solubility of the formed top coat in a 2.38% aqueous tetramethylammonium hydroxide solution, intermixing, refractive index n , and extinction coefficient k are evaluated using the following criteria.

[0093]

[Homogeneity of Top Coat Composition]

The appearance of prepared compositions is observed by the eye to evaluate the homogeneity.

15 A: Homogeneous and transparent

B: Turbidity is observed

[0094]

[Solubility in Deionized Water]

20 A composition of each example is applied on a substrate and heated at 90°C for 1 minute for drying to form a top coat. The film thickness of the obtained top coat is measured, then the top coat is immersed in deionized water at 23°C for 1 minute, and after that, the film thickness of the top coat is measured. A ratio of film thickness before and after immersion in deionized water is measured.

25 [0095]

[Solubility in Aqueous Tetramethylammonium Hydroxide Solution]

30 A composition of each example is applied on a substrate and heated at 90°C for 1 minute for drying to form a top coat. The film thickness of the obtained top coat is measured, then the top coat is immersed in a 2.38% aqueous tetramethylammonium hydroxide solution at 23°C for 1 minute, and after that, the film thickness of the top coat is measured. A ratio of film

thickness before and after immersion in the aqueous tetramethylammonium hydroxide solution is measured.

[0096]

[Intermixing]

5 A resist composition (AZ DX3200P Photoresist (9.0 cP), Merck Electronics Ltd.) is applied on a substrate, then preliminarily dried, and after that, a top coat composition of each example is applied. The resist composition and the top coat composition are further heated to form a resist film and a top coat. Cross sections of the formed resist film and top coat are
10 observed under a microscope to evaluate whether intermixing has occurred.

A: Intermixing does not occur

B: Intermixing occurs

[0097]

15 [Refractive index n and Extinction Coefficient k]

The composition of each example is applied on the substrate and heated at 90°C for 1 minute for drying to form a top coat. The refractive index n and extinction coefficient k of the resulting top coat with respect to light with a wavelength of 193 nm are measured by ellipsometer M-2000D (J.A.

20 Woollam Japan).

[0098]

Table 3 shows the obtained results.

[0099]

[Table 3]

Table 3

	Homogeneity of top coat composition	Solubility		Inter- mixing	Refractive index	Extinction coefficient
		Solubility in deionized water	Solubility in aqueous TMAH solution			
Example 1	A	94.5%	13.2%	A	1.62	0.00
Example 2	A	94.2%	10.5%	A	1.62	0.00
Example 3	A	94.4%	12.0%	A	1.62	0.00
Example 4	A	97.8%	14.0%	A	1.62	0.00
Example 5	A	90.3%	4.8%	A	1.69	0.00
Example 6	A	97.0%	14.5%	A	1.62	0.00
Compar. Ex. 1	B	99.0%	17.4%	A	1.63	0.00
Compar. Ex. 2	A	79.0%	2.6%	A	1.62	0.00
Compar. Ex. 3	A	85.4%	5.5%	B	1.62	0.00

[0100]

From this result, it is found that the top coat composition according to the present invention has homogeneity and high transparency. It is found that the top coat formed is less soluble in deionized water, while the top coat is highly soluble in a 2.38% aqueous tetramethylammonium hydroxide solution, which is used as a developer. Then, it is found that the top coat composition according to the present invention does not cause intermixing with a resist film and can achieve low refractive index n and extinction coefficient k.

[CLAIMS]

[Claim 1]

A top coat composition comprising a graft polymer (A) and a solvent (B),
the graft polymer (A) comprising a skeleton polymer (AB) moiety and a
5 side chain polymer (AG) moiety;
the side chain polymer (AG) having a cLogP of 15 to 100;
the skeleton polymer (AB) having a cLogP of 1.10 to 3.00; and,
optionally, (cLogP of the side chain polymer (AG))/(cLogP of the skeleton
polymer (AB)) being 5 to 30; or
10 optionally, the graft polymer (A) having a cLogP of 3 to 9.5.

[Claim 2]

The top coat composition according to claim 1, wherein the solvent (B)
comprises water (B1); and
optionally, the content of the solvent (B) is 75% to 99.5% by mass based
15 on a total mass of the top coat composition; or
optionally, the content of the water (B1) is 80% to 99.99% by mass
based on a total mass of the solvent (B); or
optionally, the content of the graft polymer (A) is 0.5% to 5% by mass
based on a total mass of the top coat composition.

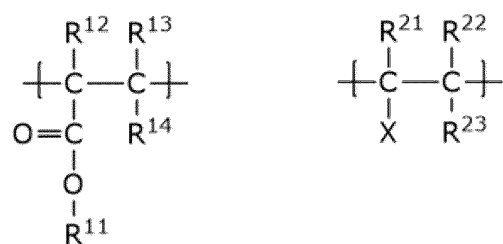
20 [Claim 3]

The top coat composition according to claim 1 or 2, wherein the side
chain polymer (AG) moiety has a number average molecular weight (Mn) of
4,000 to 35,000;
optionally, the graft polymer (A) has a mass average molecular weight
25 (Mw) of 6,000 to 100,000; or
optionally, the side chain polymer (AG) moiety has an Mw of 5,000 to
30,000; or
optionally, the skeleton polymer (AB) moiety has a Mw of 6,000 to
30,000.

30 [Claim 4]

The top coat composition according to any one of claims 1 to 3, wherein the graft polymer (A) is a polymer comprising at least one repeating unit represented by formula (a-1) or (a-2):

[C1]



(a-1)

(a-2)

wherein

R¹¹ represents hydrogen or a linear, branched, or cyclic C₁₋₃₀ hydrocarbon group, where the hydrocarbon group can be substituted with hydroxy or carboxy;

R¹² to R¹⁴ and R²¹ to R²³ each independently represent hydrogen or a linear, branched, or cyclic C₁₋₃₀ hydrocarbon group;

the hydrocarbon group each can be substituted with fluorine, hydroxy, or alkoxy;

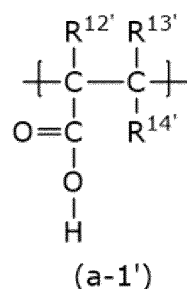
any -CH₂- in the hydrocarbon group can be substituted with -O- or -CO-, where the -CH₂- (methylene group) includes terminal methyl; and

X is the side chain polymer (AG) moiety and is a polymer moiety comprising at least one siloxane bond.

[Claim 5]

The top coat composition according to any one of claims 1 to 4, wherein the skeleton polymer (AB) moiety is a polymer comprising at least one repeating unit represented by formula (a-1'):

[C2]



wherein

$\text{R}^{12'}$ to $\text{R}^{14'}$ each independently represent hydrogen, -COOH, or a linear, branched, or cyclic C_{1-30} hydrocarbon group;

5 the hydrocarbon group each can be substituted with fluorine, hydroxy, or alkoxy; and

any -CH₂- in the hydrocarbon group can be substituted with -O- or -CO-, where the -CH₂- (methylene group) includes terminal methyl.

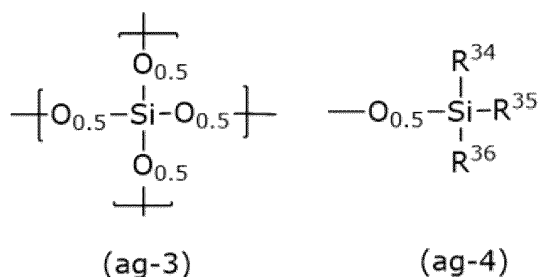
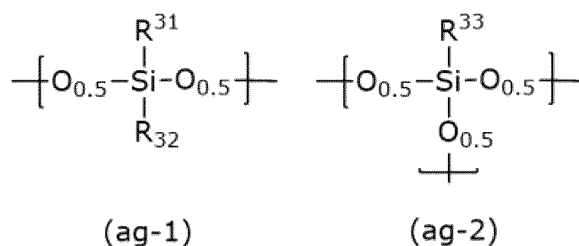
[Claim 6]

10 The top coat composition according to any one of claims 1 to 5, wherein the skeleton polymer (AB) moiety is a polymer of at least one monomer selected from the group consisting of methacrylic acid, acrylic acid, butyl acrylate, methyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, β -carboxyethyl (meth)acrylate, maleic acid, 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, a ring-opened product of glycidyl (meth)acrylate, methoxyethyl (meth)acrylate, polyalkoxyalkyl (meth)acrylate, and tetrahydrofurfuryl (meth)acrylate.

[Claim 7]

20 The top coat composition according to any one of claims 1 to 6, wherein the side chain polymer (AG) moiety is a polymer comprising at least one repeating unit represented by formula (ag-1), (ag-2), or (ag-3), and comprising a terminal group represented by formula (ag-4):

[C3]



wherein

R^{31} to R^{36} each independently represent hydrogen, a linear, branched, or cyclic C_{1-30} saturated aliphatic hydrocarbon group, or a C_{6-30} aromatic hydrocarbon group;

the aliphatic hydrocarbon group and the aromatic hydrocarbon group can each be substituted with fluorine or alkoxy; and

any $-\text{CH}_2-$ in the aliphatic hydrocarbon group and the aromatic hydrocarbon group can be substituted with $-\text{O}-$ or $-\text{NH}-$, where the $-\text{CH}_2-$ (methylene group) includes terminal methyl.

[Claim 8]

The top coat composition according to claim 7, wherein the side chain polymer (AG) moiety is linked to the skeleton polymer (AB) moiety via a linking group represented by formula (x-1):

*-D-E-F-G-# (x-1)

wherein

* denotes a site to be linked to the skeleton polymer (AB) moiety,

denotes a site to be linked to the side chain polymer (AG) moiety,

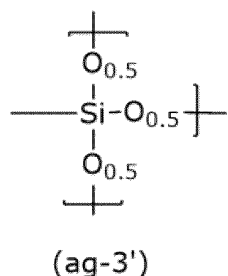
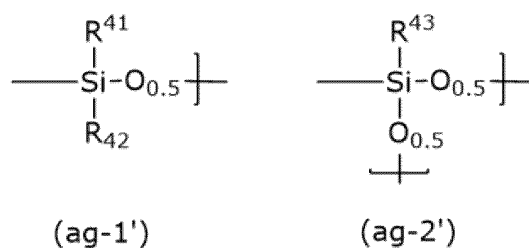
D is a single bond or $-\text{CO}-$,

E is a single bond, $-\text{O}-$, $-\text{NH}-$, or $-\text{S}-$,

F is a single bond or a divalent C₁₋₁₂ hydrocarbon group in which -CH₂- can be substituted with -O- or -NH-, and

G is represented by one of formula (ag-1'), (ag-2'), or (ag-3'):

[C4]



5

wherein

R⁴¹ to R⁴³ each independently represent hydrogen, a linear, branched, or cyclic C₁₋₃₀ saturated aliphatic hydrocarbon group, or a C₆₋₃₀ aromatic hydrocarbon group;

10

the aliphatic hydrocarbon group and the aromatic hydrocarbon group can each be substituted with fluorine or alkoxy;

any -CH₂- in the aliphatic hydrocarbon group and the aromatic hydrocarbon group can be substituted with -O- or -NH-, where the -CH₂- (methylene group) includes terminal methyl.

15

[Claim 9]

The top coat composition according to any one of claims 1 to 8, wherein the side chain polymer (AG) moiety is hydrophobic, and optionally, the skeleton polymer (AB) moiety is hydrophilic.

[Claim 10]

The top coat composition according to any one of claims 1 to 9, wherein a mass ratio (AG/A) of the side chain polymer (AG) moiety based on a total mass of the graft polymer (A) is 10.0% to 50.0% by mass.

[Claim 11]

5 The top coat composition according to any one of claims 1 to 10, wherein the solvent (B) comprises an alcohol solvent (B2); and

optionally, the content of the alcohol solvent (B2) is 0% to 5.0% by mass based on a total mass of the solvent (B).

[Claim 12]

10 The top coat composition according to any one of claims 1 to 11, which does not gel when stand still at room temperature for 12 hours, and optionally, the top coat composition has a viscosity of 1 to 100 mPa·s after standing still at room temperature for 12 hours.

[Claim 13]

15 The top coat composition according to any one of claims 1 to 12, wherein the skeleton polymer (AB) is a linear polymer, and

optionally, the graft polymer (A) is not in the form of colloid particles in the top coat composition.

[Claim 14]

20 The top coat composition according to any one of claims 1 to 13, further comprising a surfactant (C); and

optionally, further comprising a base (D); or

optionally, further comprising one or more other additives (E) selected from at least one selected from the group consisting of an acid, a lower alcohol (C₁₋₆ alcohol), a surface leveling agent, an adhesion agent, a defoamer, and a preservative.

25

[Claim 15]

The top coat composition according to claim 14, wherein

30 the content of the surfactant (C) is 0% to 5% by mass based on a total mass of the top coat composition; or

the content of the base (D) is 0% to 5% by mass based on a total mass of the top coat composition; or

the content of the one or more other additives (E) is 0% to 5% by mass based on a total mass of the top coat composition.

[Claim 16]

5 The top coat composition according to any one of claims 1 to 15, wherein the top coat composition is a liquid immersion top coat composition, and optionally, the top coat composition is a liquid immersion resist upper layer film composition; or optionally, the top coat composition is a liquid immersion ArF resist upper layer film composition; or
10 optionally, the top coat composition is a liquid immersion top anti-reflective coating composition for ArF resists.

[Claim 17]

The top coat composition according to any one of claims 1 to 16, wherein the cLogP of the graft polymer (A) is calculated by calculating a cLogP of
15 each repeating unit, multiplying the cLogP of each repeating unit by a composition ratio of each repeating unit, and summing the values obtained by the multiplication;

the cLogP of the side chain polymer (AG) moiety is calculated by multiplying a cLogP of repeating units constituting the side chain polymer (AG) moiety by a polymerization degree calculated from a number average
20 molecular weight of the side chain polymer (AG) moiety; and

the cLogP of the skeleton polymer (AB) moiety is calculated by calculating a cLogP of each repeating unit for the remainder of repeating units excluding the repeating units of the side chain polymer (AG) from the
25 graft polymer (A), multiplying the cLogP of each repeating unit by a composition ratio of each repeating unit, and summing the values obtained by the multiplication.

[Claim 18]

30 The top coat composition according to any one of claims 1 to 17, wherein a top coat formed from the top coat composition does not dissolve in water, and

optionally, the top coat formed from the top coat composition dissolves in a 2.38% aqueous tetramethylammonium hydroxide solution, or

optionally, intermixing does not occur at an interface between the top coat formed from the top coat composition and a resist film.

5 [Claim 19]

The top coat composition according to any one of claims 1 to 18, wherein the top coat formed from the top coat composition has a refractive index n with respect to light with a wavelength of 193 nm of 1.40 to 1.80, and

optionally, the top coat has an extinction coefficient k of 0.00 to 0.25.

10 [Claim 20]

A method for producing a resist pattern using the top coat composition according to any one of claims 1 to 19.

[Claim 21]

A method for producing a resist pattern, comprising the steps of:

15 (1) applying a photosensitive resin composition above a substrate via or not via at least one intermediate layer to form a resist film;

(2) applying the top coat composition according to any one of claims 1 to 19 directly on the resist film to form a top coat;

(3) exposing the top coat and the resist film to radiation; and

20 (4) developing the top coat and the resist film,

optionally, the method further comprising any one of the following steps:

(2-2) immersing a substrate having the top coat and the resist film in an immersion liquid; or

(5) washing the developed top coat and resist film with a rinse solution.

25 [Claim 22]

The method for producing a resist pattern according to claim 21, wherein the photosensitive resin composition is a chemically amplified photosensitive resin composition, and optionally, ArF is used for exposure to light.

30 [Claim 23]

A method for producing a device, comprising the method for producing a resist pattern according to any one of claims 20 to 22.

[Claim 24]

The method for producing a device according to claim 23, further comprising performing etching a resist pattern produced by the method according to any one of claims 20 to 22 as a mask to process a substrate.

5

[Claim 25]

The method for producing a device according to claim 23 or 24, further comprising forming wiring on a processed substrate.