

ION IMPLANTATION THICK FILM RESIST COMPOSITION,
METHOD FOR MANUFACTURING PROCESSED SUBSTRATE USING
THE SAME AND METHOD FOR MANUFACTURING DEVICE USING
THE SAME

5

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

[0001] The present invention relates to an ion
10 implantation thick film resist composition, a method for
manufacturing a processed substrate using the same
and a method for manufacturing a device using the
same.

15 BACKGROUND ART

[0002] In the manufacture of semiconductor devices, an
ion implantation process is employed in which impurity
ions are introduced into a semiconductor substrate using
a resist pattern as a mask. The impurity ions are
20 implanted at high energy using an ion implanter. As
designs become finer and the amount of ion implantation
tend to increase, resist patterns used in the ion
implantation process are required to be thicker and more
rectangular, and to have higher heat resistance, or the
25 like.

[0003] Thick film resist compositions have been proposed
for processes such as plating processes, etching
processes (for example, Patent Document 1), but there
is still a demand for improved resolution and
30 rectangularity.

Although thick film resist compositions have been
proposed for high-energy ion implantation processes and
the like, improvements in resolution and the like are still
required (for example, Patent Document 2).

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PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004] [Patent document 1] JP 2007-206425 A

[Patent document 2] WO 2004/104702

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SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] The present inventors have considered that there
10 are still one or more problems with ion implantation
resist compositions and their uses that require
improvement. They include, for example, the following:
resist pattern having sufficiently high rectangularity
cannot be obtained; sufficient resolution cannot be
15 obtained; ion implantation resistance of the resist
pattern is insufficient; transmittance of the resist film is
low; a resist pattern with a high aspect ratio cannot be
formed; and heat resistance of the resist pattern is
insufficient.

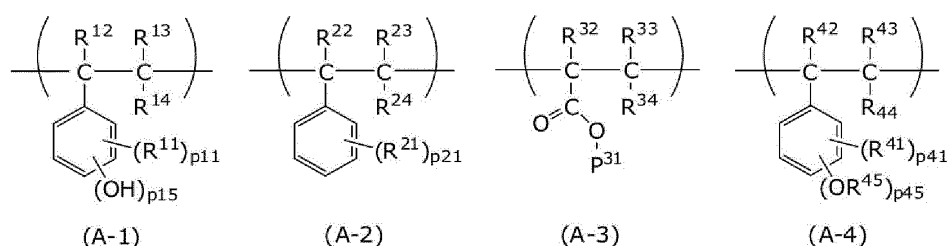
20 The present invention has been made based on the
technical background as described above, and provides
an ion implantation thick film resist composition and a
method for manufacturing a processed substrate using
the same.

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MEANS FOR SOLVING THE PROBLEMS

[0006] The ion implantation thick film resist composition
according to the present invention comprises a polymer
(A), a photoacid generator (B) and a solvent (C),
30 wherein,
the film thickness of the resist film formed from the
composition is 1.0 to 50 μm ;
the mass average molecular weight of the polymer (A) is
5,000 to 19,000; and
35 the polymer (A) comprises at least one of the repeating
unit represented by formulae (A-1), (A-2), (A-3) and (A-

4):



wherein

R^{11} , R^{21} , R^{41} and R^{45} are each independently C_{1-5} alkyl (wherein methylene in the alkyl can be replaced with oxy);

R^{12} , R^{13} , R^{14} , R^{22} , R^{23} , R^{24} , R^{32} , R^{33} , R^{34} , R^{42} , R^{43} and R^{44} are each independently hydrogen, C_{1-5} alkyl, C_{1-5} alkoxy or $-COOH$;

p_{11} is 0 to 4, p_{15} is 1 to 2, and $p_{11} + p_{15} \leq 5$;

p_{21} is 0 to 5;

p_{41} is 0 to 4, p_{45} is 1 to 2, and $p_{41} + p_{45} \leq 5$;

P^{31} is C_{4-20} alkyl (wherein a part or all of the alkyl can form a ring, a part or all of H in the alkyl can be replaced with halogen, and methylene in the alkyl can be replaced with oxy or carbonyl).

[0007] The method for manufacturing a processed substrate according to the present invention comprises the following steps:

manufacturing a resist pattern using the above-described ion implantation thick film resist composition; and

performing an ion implantation using the resist pattern as a mask, or

processing the underlayer of the resist pattern using the resist pattern as a mask to form a underlayer pattern, and performing an ion implantation using the underlayer pattern as a mask.

[0008] The method for manufacturing a device according to the present invention comprises the above-described method for manufacturing a processed substrate.

EFFECTS OF THE INVENTION

[0009] The inventors have considered as follows in the course of reaching the present invention. A thick resist film must be formed because the resist pattern itself, which is a mask, is also shaved by the implantation of ionized impurities. In order to form a thick film, the film must have high transparency. A thicker film requires higher rectangularity. Furthermore, since the ion implantation resist pattern generates heat during the process, it must also have excellent heat resistance. As a result of intensive studies, the present inventors have obtained the composition of the present invention.

According to the present invention, one or more of the following effects are provided:

A resist pattern with high rectangularity is obtained; a resist film with high resolution is obtained; a resist pattern has high resistance to ion implantation; transmittance of the resist film is high; a resist pattern with high aspect ratio is formed; and heat resistance of the resist pattern is high.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] [Figure 1] Schematic view showing cross-sectional shape of a trench pattern.

[Figure 2] Schematic view showing cross-sectional shapes of resist patterns having different W_t / W_b .

DETAILED DESCRIPTION OF THE INVENTION

MODE FOR CARRYING OUT THE INVENTION

[0011] [Definition]

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

The singular form includes the plural form and

"one" or "that" means "at least one". An element of a concept can be expressed by a plurality of species, and when the amount (for example, mass % or mol %) is described, it means sum of the plurality of species.

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

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

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

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

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

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

35 [0012] Hereinafter, embodiments of the present invention are described in detail.

[0013] <Ion implantation thick film resist composition>

5 The ion implantation thick film resist composition according to the present invention (hereinafter referred to as the composition) comprises a polymer (A) having a certain structure, a photoacid generator (B) and a solvent (C).

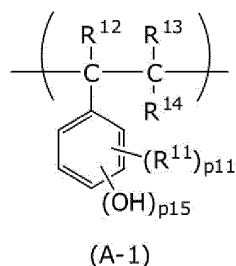
10 The composition according to the present invention is a thin film resist composition. In the present invention, the thin film means a film having a thickness of 1.0 to 50 μm , preferably 1.2 to 30 μm (more preferably 1.5 to 20 μm ; further preferably 2 to 10 μm). The viscosity of the composition according to the present invention is preferably 10 to 1,000 $\text{mPa}\cdot\text{s}$, more preferably 12 to 500 $\text{mPa}\cdot\text{s}$. The viscosity is measured at 25°C with a capillary viscometer.

15 The composition according to the present invention is more preferably a KrF chemically amplified resist composition; more preferably a KrF positive type chemically amplified resist composition.

20 [0014] Polymer (A)

The composition according to the present invention comprises a polymer (A). The polymer (A) comprises at least one of the repeating units represented by the following formulae (A-1), (A-2), (A-3) and (A-4). The polymer (A) reacts with an acid to increase its solubility in an alkaline aqueous solution. This kind of polymer has, for example, an acid group protected by a protecting group, and when an acid is added from outside, the protecting group is eliminated and the solubility in an alkaline aqueous solution increases.

30 [0015] The formula (A-1) is as follows:



wherein

R^{11} is each independently C_{1-5} alkyl (wherein methylene in the alkyl can be replaced with oxy); preferably methyl or ethyl; more preferably methyl. In the present invention, the expression "methylene in the alkyl can be replaced by oxy" means that oxy can be present between carbon atoms in the alkyl, and it is not intended that the terminal carbon in the alkyl becomes oxy, i.e., have alkoxy or hydroxy.

R^{12} , R^{13} and R^{14} are each independently hydrogen, C_{1-5} alkyl, C_{1-5} alkoxy or $-\text{COOH}$; preferably hydrogen or methyl; more preferably hydrogen.

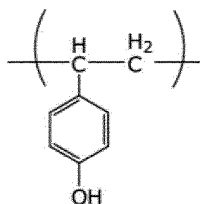
$p11$ is 0 to 4; preferably 0 or 1; more preferably 0.

$p15$ is 1 to 2; preferably 1.

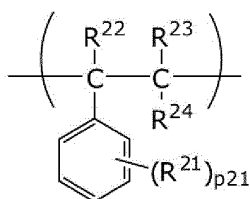
$p11 + p15 \leq 5$ is satisfied.

[0016] The polymer (A) can contain a plurality of types of repeating units represented by the formula (A-1). For example, it is possible for the polymer to have a structural unit of $p15 = 1$ and a structural unit of $p15 = 2$ at a ratio of 1 : 1. In this case, it becomes $p15 = 1.5$ as a whole. Hereinafter, unless otherwise specified, the same applies to the numbers for representing polymer in the present invention.

[0017] An exemplified embodiment of the formula (A-1) includes the following:



[0018] The formula (A-2) is as follows:



(A-2)

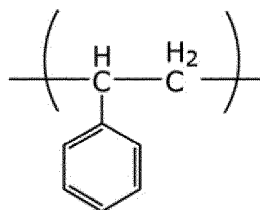
wherein

5 R^{21} is each independently C_{1-5} alkyl (wherein methylene in the alkyl can be replaced with oxy); preferably methyl, ethyl, t-butyl or t-butoxy; more preferably methyl or ethyl; further preferably methyl.

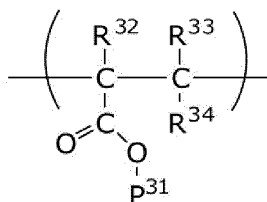
10 R^{22} , R^{23} and R^{24} are each independently hydrogen, C_{1-5} alkyl, C_{1-5} alkoxy or $-COOH$; preferably hydrogen or methyl; more preferably hydrogen.

p_{21} is 0 to 5; preferably 0, 1, 2, 3, 4 or 5; more preferably 0 or 1; further preferably 0.

15 [0019] An exemplified embodiment of the formula (A-2) includes the following:



[0020] The formula (A-3) is as follows:



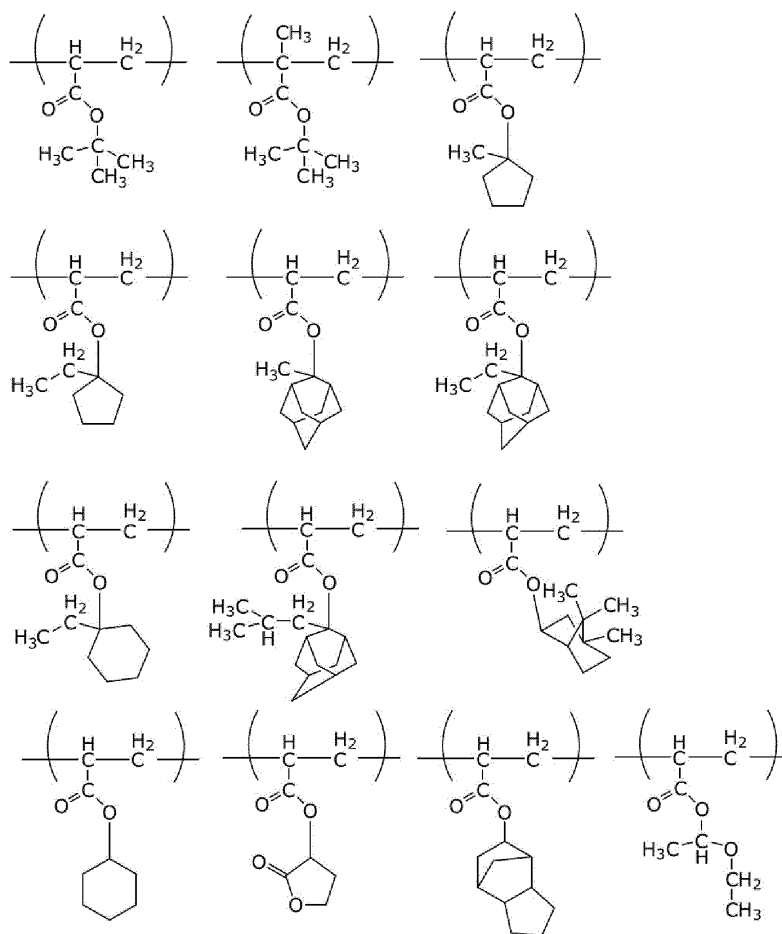
(A-3)

wherein

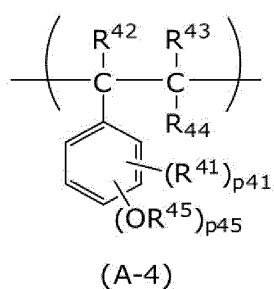
R^{32} , R^{33} and R^{34} are each independently hydrogen, C_{1-5} alkyl, C_{1-5} alkoxy or $-COOH$; preferably hydrogen, methyl, ethyl, t-butyl, methoxy, t-butoxy or $-COOH$; more preferably hydrogen or methyl; further preferably hydrogen.

P^{31} is C_{4-20} alkyl. A part or all of the alkyl can form a ring, a part or all of H in the alkyl can be replaced with halogen, and methylene in the alkyl can be replaced with oxy or carbonyl. The alkyl moiety of P^{31} is preferably branched or cyclic. When the C_{4-20} alkyl in P^{31} is replaced with halogen, it is preferable that all are replaced, and the halogen that replaces is preferably F or Cl; more preferably F. It is a preferred embodiment of the present invention that H of the C_{4-20} alkyl in P^{31} is not replaced with any halogen. P^{31} is preferably methyl, isopropyl, t-butyl, cyclopentyl, methylcyclopentyl, ethylcyclopentyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, adamantyl, methyladamantyl or ethyladamantyl; more preferably t-butyl, ethylcyclopentyl, ethylcyclohexyl or ethyladamantyl; further preferably t-butyl, ethylcyclopentyl or ethyladamantyl; further more preferably t-butyl.

[0021] Exemplified embodiments of the formula (A-3) include the following:



[0022] The formula (A-4) is as follows:



wherein

5 R⁴¹ is each independently C₁₋₅ alkyl (wherein methylene in the alkyl can be replaced with oxy); preferably methyl, ethyl or t-butyl; more preferably methyl.
R⁴⁵ is each independently C₁₋₅ alkyl (wherein methylene

in the alkyl can be replaced with oxy); preferably methyl, t-butyl or $-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}_3$.

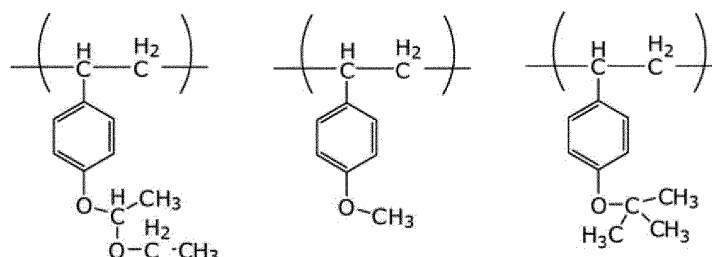
R^{42} , R^{43} and R^{44} are each independently hydrogen, C_{1-5} alkyl, C_{1-5} alkoxy or $-\text{COOH}$; preferably hydrogen or methyl; more preferably hydrogen.

p_{41} is 0 to 4; preferably 0 or 1; more preferably 0.

p_{45} is 1 to 2; preferably 1.

$p_{41} + p_{45} \leq 5$ is satisfied.

[0023] Exemplified embodiments of the formula (A-4) include the following:



[0024] These structural units are appropriately blended according to the purpose. It is a preferred embodiment that the constituent is made so that the rate of increase in solubility in the alkaline aqueous solution by an acid becomes appropriate.

n_{A-1} , n_{A-2} , n_{A-3} and n_{A-4} , which are the numbers of repeating units represented by the formulae (A-1), (A-2), (A-3) and (A-4) in the polymer (A), are described below:

$n_{A-1} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 40 to 80%; more preferably 50 to 80%; further preferably 55 to 75%; further more preferably 55 to 65%.

$n_{A-2} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0 to 40%; more preferably 0 to 30%; further preferably 5 to 25%; further more preferably 15 to 25%.

$n_{A-3} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 10 to 50%; more preferably 10 to 40%; further preferably 15 to 35%; further more preferably 15 to 25%.

$n_{A-4} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0 to

40%; more preferably 0 to 30%; further preferably 0 to 10%; further more preferably 0 to 5%. It is also a preferred embodiment of the present invention that n_{A-4} is 0. A preferred embodiment includes the following:

5
$$\begin{aligned} n_{A-1} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) &= 40 \text{ to } 80\%, \\ n_{A-2} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) &= 0 \text{ to } 40\%, \\ n_{A-3} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) &= 10 \text{ to } 50\%, \text{ and} \\ n_{A-4} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) &= 0 \text{ to } 40\%. \end{aligned}$$

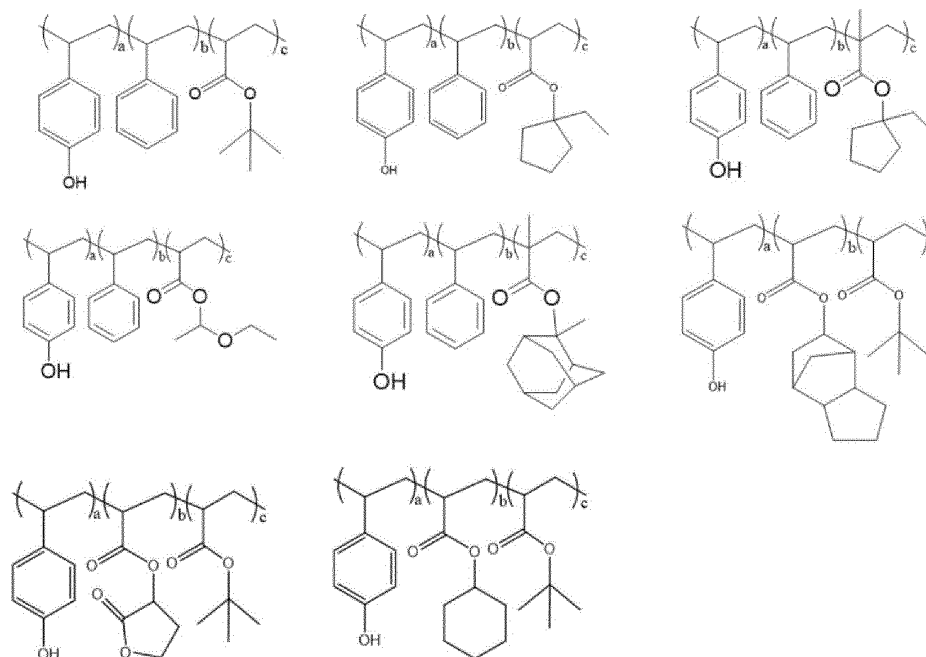
10 One embodiment of the present invention is that $n_{A-3} > 0$ and $n_{A-4} = 0$.

[0025] The polymer (A) can also contain a further repeating unit other than the repeating units represented by the formulae (A-1), (A-2), (A-3) and (A-4).

15 The further repeating unit is preferably a repeating unit comprising arylcarbonyl.

The content of the further repeating unit contained in the polymer (A) is preferably 0 to 10 mass parts; more preferably 0 to 5 mass parts; further preferably 0 to 1 mass parts, with respect to 100 mass parts of the polymer (A). It is also a preferred embodiment of the polymer (A) to contain no further repeating unit. In other words, it is also a preferred embodiment to contain no repeating unit comprising arylcarbonyl.

20
25 [0026] Exemplified embodiments of the polymer (A) include the following:

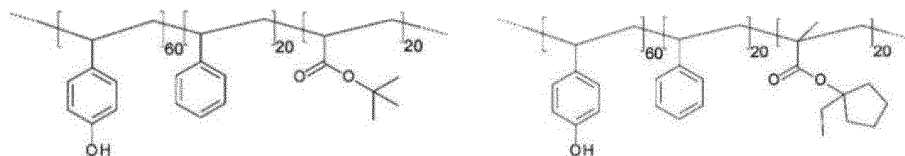


[0027] The mass average molecular weight (hereinafter referred to as Mw) of the polymer (A) is 5,000 to 19,000; more preferably 8,000 to 19,000; further preferably 10,000 to 19,000; further more preferably 11,000 to 13,000. Without wishing to be bound by theory, it can be thought that due to the polymer (A) having this Mw, it becomes possible to form a resist pattern with good rectangularity or resolution from the composition of the present invention.

In the present invention, Mw can be measured by gel permeation chromatography (GPC). In the measurement, it is a preferable example that a GPC column at 40 degrees Celsius, an elution solvent of tetrahydrofuran at 0.6 mL/min and monodisperse polystyrene as a standard are used.

[0028] The following is described for explanation. In the composition of the present invention, the polymer (A) can be used in any combination of any of two or more as long as they are represented by the above formula. For example, a composition containing the following two

types of polymer (A) is also one embodiment of the present invention:



5 The same applies to the composition of the present invention in the following description unless otherwise specified.

The polymer (A) contained in the composition according to the present invention consists of one or two types of polymer; preferably, the polymer (A) consists of one type of polymer. Variations in Mw distribution and polymerization are allowed.

[0029] The content of the polymer (A) is preferably 10 to 40 mass %; more preferably 12 to 38 mass %; further preferably 15 to 36 mass %, based on the composition.

15 The composition according to the present invention can contain a polymer other than the polymer (A), but an embodiment in which no polymer other than the polymer (A) is one preferred embodiment.

[0030] Photoacid generator (B)

20 The composition according to the present invention comprises a photoacid generator (B). The photoacid generator (B) releases an acid upon irradiation with light. Preferably, the acid derived from the photoacid generator (B) acts on the polymer (A) to increase the solubility of the polymer (A) in an alkaline aqueous solution. For example, when the polymer (A) has an acid group protected by a protecting group, the protecting group is released by an acid. The photoacid generator (B) used in the composition according to the present invention can be selected from those

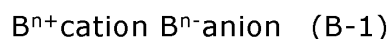
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30 conventionally known.

[0031] Upon exposure, the photoacid generator (B)

releases an acid having an acid dissociation constant pK_a (H_2O) of -20 to 1.4; more preferably -16 to 1.4; further preferably -16 to 1.2; further more preferably -16 to 1.1.

5 [0032] The photoacid generator (B) is preferably represented by the formula (B-1).



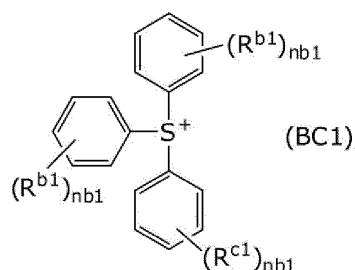
wherein

10 the B^{n+} cation is a cation represented by the formula (BC1), a cation represented by the formula (BC2) or a cation represented by the formula (BC3); preferably the cation represented by the formula (BC1) or the cation represented by the formula (BC2); more preferably the cation represented by the formula (BC1).
15 The B^{n+} cation is n valent as a whole, and n is 1 to 3. The B^{n-} anion is a sulfonate anion, and preferably an anion represented by the formula (BA1), an anion represented by the formula (BA2), an anion represented by the formula (BA3) or an anion represented by the formula (BA4); more preferably an anion represented by the formula (BA3). The B^{n-} anion is n valent as a whole.

n is preferably 1 or 2; more preferably 1.

20 Without wishing to be bound by theory, it is thought to become possible, using the photoacid generator (B) as described above, to control a large amount of the photoacid generator (B) is present near the bottom of the resist film when it is formed and to control the shape of the pattern to be a rectangular shape. In a positive type resist, the exposed area is
25 solubilized, but the amount of light decreases while reaching the bottom of the resist film; therefore, it is effective to control the pattern shape by the amount of the photoacid generator (B).
30

[0033] The formula (BC1) is as follows:

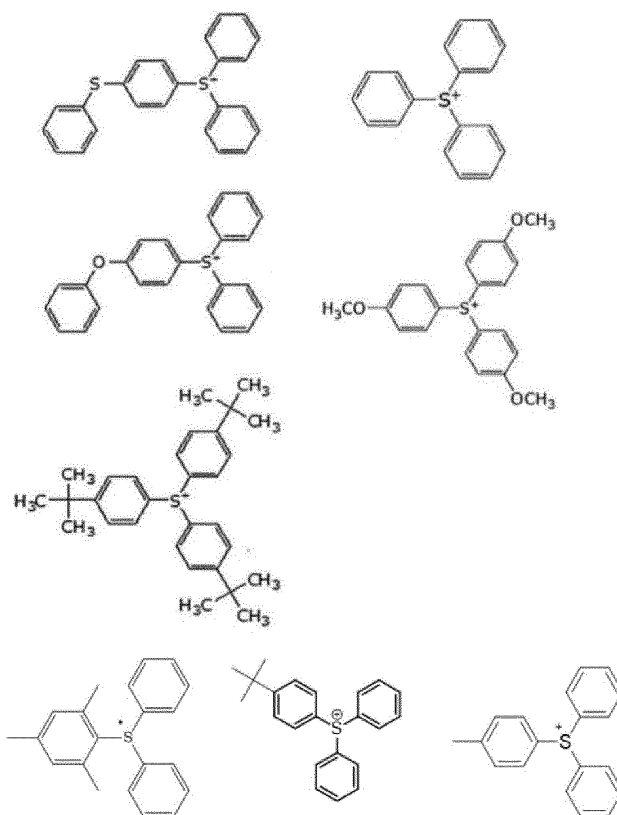


wherein

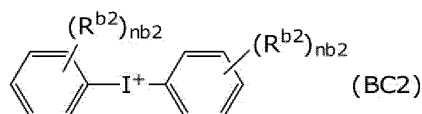
R^{b1} is each independently C_{1-6} alkyl, C_{1-6} alkoxy, C_{6-12} aryl, C_{6-12} arylthio or C_{6-12} aryloxy; preferably methyl, ethyl, t-butyl, methoxy, ethoxy, phenylthio or phenyloxy; more preferably t-butyl, methoxy, ethoxy, phenylthio or phenyloxy.

$nb1$ is each independently 0, 1, 2 or 3; preferably 0 or 1; more preferably 0.

[0034] Exemplified embodiments of the formula (BC1) include the following:



[0035] The formula (BC2) is as follows:



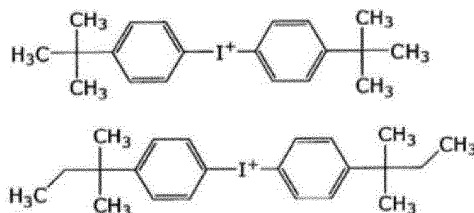
wherein

R^{b2} is each independently C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl; preferably alkyl having a C_{4-6} branched structure.

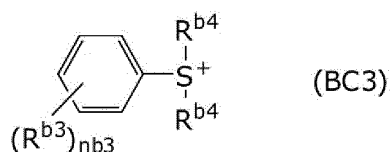
R^{b2} in the formula can be identical to or different from each other, and one in which they are identical to each other is more preferable. R^{b2} is further preferably *t*-butyl or 1,1-dimethylpropyl; further more preferably *t*-butyl.

$nb2$ is each independently 0, 1, 2 or 3; preferably 1.

[0036] Exemplified embodiments of the formula (BC2) include the following:



[0037] The formula (BC3) is as follows:



wherein

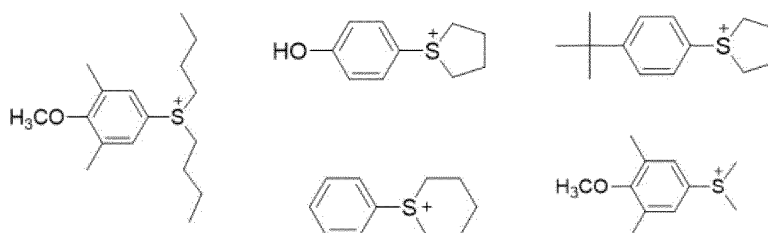
R^{b3} is each independently hydroxy, C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl; preferably methyl, ethyl, methoxy or ethoxy; more preferably methyl or methoxy.

R^{b4} is each independently C_{1-6} alkyl; preferably methyl, ethyl, propyl or butyl. Two R^{b4} can be bonded to each other to form a ring structure, and when a ring is formed, it is preferred to form a 5- or 6-membered

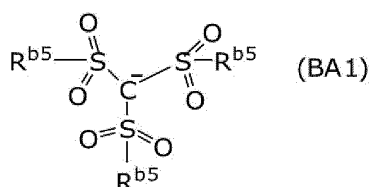
alicyclic.

nb3 is each independently 0, 1, 2 or 3; preferably 1, 2 or 3; more preferably 1 or 3.

[0038] Exemplified embodiments of the formula (BC3) include the following:



[0039] The formula (BA1) is as follows:



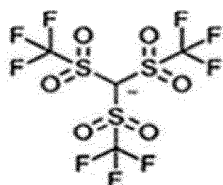
wherein

10 R^{b5} is each independently fluorine-substituted C_{1-6} alkyl, fluorine-substituted C_{1-6} alkoxy, or C_{1-6} alkyl. For example, $-CF_3$ means that all of hydrogen in methyl (C_1) are replaced with fluorine. In the present invention, the fluorine substitution means that a part or all of
15 hydrogen existing in the alkyl moiety are replaced with fluorine, and more preferably all of hydrogen are replaced with fluorine.

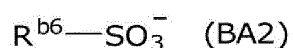
The alkyl moiety of R^{b5} is preferably methyl, ethyl or t-butyl; more preferably methyl.

20 R^{b5} is preferably fluorine-substituted alkyl; more preferably $-CF_3$.

[0040] An exemplified embodiment of the formula (BA1) includes the following:



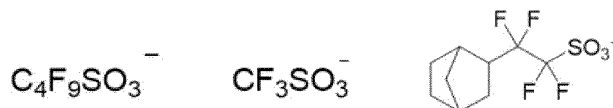
[0041] The formula (BA2) is as follows:



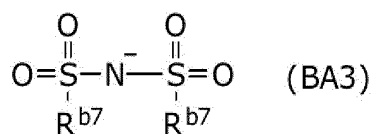
wherein

5 R^{b6} is fluorine-substituted C_{1-10} alkyl, fluorine-substituted C_{1-6} alkoxy, fluorine-substituted C_{6-12} aryl, fluorine-substituted C_{2-12} acyl, or fluorine-substituted C_{6-12} alkoxyaryl; preferably fluorine-substituted C_{1-10} alkyl. The alkyl moiety of R^{b6} is preferably linear or
10 cyclic. R^{b6} is preferably fluorine-substituted C_{1-6} alkyl; more preferably fluorine-substituted C_{2-6} alkyl.

[0042] Exemplified embodiments of the formula (BA2) include the following:



15 [0043] The formula (BA3) is as follows:

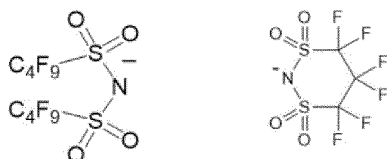


wherein

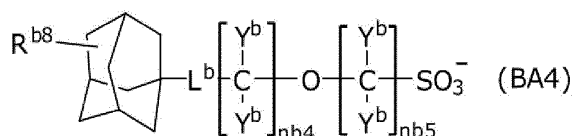
R^{b7} is each independently fluorine-substituted C_{1-6} alkyl, fluorine-substituted C_{1-6} alkoxy, fluorine-substituted C_{6-12} aryl, fluorine-substituted C_{2-12} acyl, or fluorine-substituted C_{6-12} alkoxyaryl; preferably fluorine-substituted C_{2-6} alkyl. Two R^{b7} can be bonded to each
20 other to form a fluorine-substituted heterocyclic structure. The heterocyclic structure is preferably a

saturated ring. The heterocyclic structure, including N and S, is preferably a 5- to 8-membered monocyclic structure; more preferably a 5- or 6-membered ring; further preferably a 6-membered ring.

- 5 [0044] Exemplified embodiments of the formula (BA3) include the following:



- [0045] The formula (BA4) is as follows:



- 10 wherein
 R^{b8} is hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy or hydroxy;
 preferably hydrogen, methyl, ethyl, methoxy or hydroxy;
 more preferably hydrogen or hydroxy.
 L^b is methylene, ethylene, carbonyl, oxy or carbonyloxy;
 15 preferably ethylene or carbonyl.
 Y^b is each independently hydrogen or fluorine;
 preferably, one or more of Y^b is fluorine.
 $nb4$ is an integer of 0 to 10; preferably 0, 1 or 2.
 $nb5$ is an integer of 0 to 21; preferably 4, 5 or 6.

- 20 [0046] Exemplified embodiments of the formula (BA4) include the following:



- [0047] The molecular weight of the photoacid generator (B) is preferably 300 to 1,200; more preferably 400 to 900.

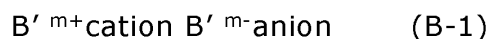
- [0048] The content of the photoacid generator (B) is

preferably 0.3 to 4 mass parts; more preferably 0.4 to 2 mass parts; further preferably 0.5 to 2 mass parts, with respect to 100 mass parts of the polymer (A). Without wishing to be bound by theory, it is thought that because the content of the photoacid generator (B) is within the above range, a resist pattern with better resolution can be formed.

[0049] The composition according to the present invention can contain a photoacid generator other than the photoacid generator (B), and examples thereof include a photoacid generator (B') represented by the following formula (B'-1). In the present invention, the photoacid generator (B') is different from the photoacid generator (B). As a preferred embodiment of the present invention, the acid that directly acts on the polymer (A) is an acid released not from the photoacid generator (B') but from the photoacid generator (B).

[0050] As a preferred embodiment of the present invention, the cation derived from the photoacid generator (B') reacts with the anion portion derived from the photoacid generator (B) and functions as a quencher. The photoacid generator (B') functions as a quencher that suppresses the diffusion of the acid derived from the photoacid generator (B), which generated in the exposed area.

[0051] The photoacid generator (B') is represented by the formula (B'-1):



wherein

the $B' \text{ } ^{m+}\text{cation}$ is a cation represented by the above-described formula (BC1) or the cation represented by the formula (BC2). Preferred embodiments are also the same as described above.

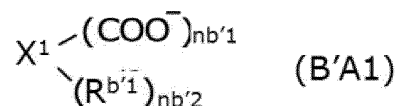
The $B' \text{ } ^{m+}\text{cation}$ is m valent as a whole, and m is 1 to 3.

The $B' \text{ } ^{m-}\text{anion}$ is an anion represented by the

formula (B'A1) or an anion represented by the formula (B'A2). The B' ^{m-}anion is m valent as a whole.

m is preferably 1 or 2; more preferably 1.

[0052] The formula (B'A1) is as follows:



5

wherein

X¹ is a C₁₋₂₀ hydrocarbon or a single bond,

R^{b'1} is each independently hydrogen, hydroxy, C₁₋₆ alkyl or C₆₋₁₀ aryl,

10 nb'1 is 1, 2 or 3, and

nb'2 is 0, 1 or 2.

[0053] When X¹ is a hydrocarbon, it can be any one of linear, branched or cyclic, preferably linear or cyclic. In the case of linear, it is preferably C₁₋₄ (more preferably C₁₋₂), and preferably has one double bond in the chain or is a saturated one. When it is cyclic, it can be a monocyclic aromatic one, or a saturated monocyclic or polycyclic one. In the case of monocyclic, a 6-

15

20

membered ring is preferred, and in the case of polycyclic, adamantane ring is preferred.

X¹ is preferably methyl, ethyl, propyl, butyl, ethane, phenyl, cyclohexane, adamantane or a single bond; more preferably methyl, phenyl, cyclohexane or a single bond; further preferably phenyl or a single bond; further more preferably phenyl.

25

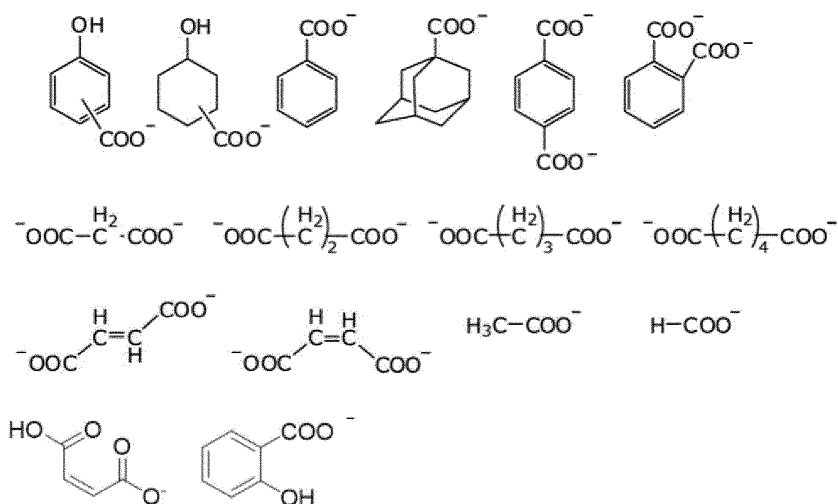
nb'1 is preferably 1 or 2; more preferably 1.

nb'2 is preferably 0 or 1; more preferably 1.

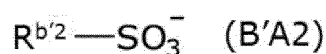
R^{b'1} is preferably hydroxy, methyl, ethyl, 1-propyl, 2-propyl, t-butyl or phenyl; more preferably hydroxy.

30 [0054] When X¹ is a single bond, R^{b'1} is preferably hydrogen. When in (B'A1), X¹ is a single bond, R^{b'1} is hydrogen and nb'1=nb'2=1, an anion that is H-COO⁻ is represented.

[0055] Exemplified embodiments of the formula (B'A1) include the following:



[0056] The formula (B'A2) is as follows:



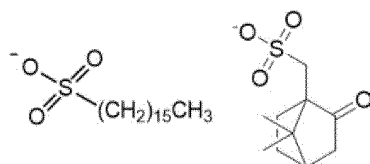
5

wherein

10 $\text{R}^{b/2}$ is C_{1-20} alkyl (wherein a part or all of the alkyl can form a ring, and $-\text{CH}_2-$ in the alkyl can be replaced with $-\text{C}(=\text{O})-$). $\text{R}^{b/2}$ is preferably C_{3-13} alkyl; more preferably C_{5-12} alkyl; further preferably C_{8-12} alkyl; further more preferably C_{10} alkyl. The alkyl of $\text{R}^{b/2}$ preferably a part or all thereof forms a ring; more preferably a part thereof forms a ring. Preferably, one or more (more preferably one) $-\text{CH}_2-$ in the alkyl of $\text{R}^{b/2}$ is replaced with $-\text{C}(=\text{O})-$.

15

[0057] Exemplified embodiments of the formula (B'A2) include the following:



[0058] Upon exposure, the photoacid generator (B')

releases an acid with an acid dissociation constant $pK_a(H_2O)$ of preferably 1.5 to 8; more preferably 1.5 to 5.

[0059] The molecular weight of the photoacid generator (B') is preferably 300 to 1,400; more preferably 300 to 1,200.

[0060] The content of the photoacid generator (B') is preferably 0.01 to 5 mass %; more preferably 0.03 to 1 mass %; further preferably 0.05 to 1 mass %; further more preferably 0.5 to 1 mass %, based on the polymer (A). It is also a preferred embodiment of the present invention that no photoacid generator (B') is contained.

[0061] Solvent (C)

The composition according to the present invention comprises a solvent (C). The solvent is not particularly limited as long as it can dissolve each component to be mixed.

Exemplified embodiments of the solvent include water, n-pentane, i-pentane, n-hexane, i-hexane, n-heptane, i-heptane, 2,2,4-trimethylpentane, n-octane, i-octane, cyclohexane, methylcyclohexane, benzene, toluene, xylene, ethylbenzene, trimethylbenzene, methylethylbenzene, n-propylbenzene, i-propylbenzene, diethylbenzene, i-butylbenzene, triethylbenzene, di-i-propylbenzene, n-amyl naphthalene, trimethylbenzene, methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, sec-butanol, t-butanol, n-pentanol, i-pentanol, 2-methylbutanol, sec-pentanol, t-pentanol, 3-methoxybutanol, n-hexanol, 2-methylpentanol, sec-hexanol, 2-ethylbutanol, sec-heptanol, heptanol-3, n-octanol, 2-ethylhexanol, sec-octanol, n-nonyl alcohol, 2,6-dimethylheptanol-4, n-decanol, sec-undecyl alcohol, trimethyl nonyl alcohol, sec-tetradecyl alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol, methylcyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol, phenylmethyl carbinol, diacetone alcohol,

cresol, ethylene glycol, propylene glycol, 1,3-butylene glycol, pentanediol-2,4,2-methylpentanediol-2,4, hexanediol-2,5, heptanediol-2,4,2-ethylhexanediol-1,3, diethylene glycol, dipropylene glycol, triethylene glycol, 5 tripropylene glycol, glycerin, acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, diethyl ketone, methyl i-butyl ketone, methyl n-pentyl ketone, ethyl n-butyl ketone, methyl n-hexyl ketone, di- i-butyl ketone, trimethylnonanone, cyclohexanone, 10 cyclopentanone, methylcyclohexanone, 2,4-pentanedione, acetonylacetone, diacetone alcohol, acetophenone, fenthion, ethyl ether, i-propyl ether, n-butyl ether (di-n-butyl ether, DBE), n-hexyl ether, 2-ethylhexyl ether, ethylene oxide, 1,2-propylene oxide, 15 dioxolane, 4-methyl dioxolane, dioxane, dimethyl dioxane, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, 20 ethylene glycol mono-2-ethyl butyl ether, ethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol di-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxytriglycol, tetraethylene glycol di-n-butyl ether, propylene glycol monomethyl ether (PGME), propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, diethyl carbonate, methyl acetate, ethyl acetate, γ -butyrolactone, γ -valerolactone, 35 n-propyl acetate, i-propyl acetate, n-butyl acetate (normal butyl acetate, nBA), i-butyl acetate, sec-butyl

acetate, n-pentyl acetate, sec-pentyl acetate, 3-methoxybutyl acetate, methylpentyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, benzyl acetate, cyclohexyl acetate, methyl cyclohexyl acetate, n-nonyl acetate, methyl acetoacetate, ethyl acetoacetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl acetate, diethylene glycol mono-n-butyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, propylene glycol monobutyl ether acetate, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, glycol diacetate, methoxytriglycol acetate, ethyl propionate, n-butyl propionate, i-amyl propionate, diethyl oxalate, di-n-butyl oxalate, methyl lactate, ethyl lactate (EL), γ -butyrolactone, n-butyl lactate, n-amyl lactate, diethyl malonate, dimethyl phthalate, diethyl phthalate, propylene glycol 1-monomethyl ether 2-acetate (PGMEA), propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, N-methylformamide, N,N-dimethylformamide, N,N-diethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, N-methylpropionamide, N-methyl pyrrolidone, dimethyl sulfide, diethyl sulfide, thiophene, tetrahydrothiophene, dimethyl sulfoxide, sulfolane, and 1,3-propane sultone. These solvents can be used alone or in combination of any two or more of these.

The solvent (C) is preferably propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, ethyl lactate, n-butyl acetate, n-butyl ether, 2-heptanone, cyclohexanone, or any combination of any of these; more preferably PGME, EL, nBA, DBE, or any mixture of any of these; further preferably PGME, EL, or any mixture of any of these; further more preferably a

mixture of PGME and EL. When two types are mixed, the mass ratio of the first solvent to the second solvent is preferably 95 : 5 to 5 : 95 (more preferably 90 : 10 to 10 : 90; further preferably 80 : 20 to 20 : 80).

5 [0062] In relation to other layers or films, it is also one embodiment that the solvent (C) substantially contains no water. For example, the amount of water in the whole solvent (C) is preferably 0.1 mass % or less; more preferably 0.01 mass % or less; further preferably
10 0.001 mass % or less. It is also a preferable embodiment that the solvent (C) contains no water (0 mass %).

[0063] The content of the solvent (C) is preferably 50 to 90 mass %; more preferably 60 to 88 mass %; further
15 preferably 65 to 85 mass %, based on the composition. By increasing or decreasing the amount of the solvent occupying in the whole composition, the film thickness after film formation can be controlled.

[0064] Basic compound (D)
20 The composition according to the present invention can further contain a basic compound (D). The basic compound has the effect of suppressing the diffusion of the acid generated in the exposed area and the effect of suppressing the deactivation of the acid on the surface
25 of the resist film by the amine component contained in the air.

[0065] The basic compound (D) is preferably ammonia, C₁₋₁₆ primary aliphatic amine, C₂₋₃₂ secondary aliphatic amine, C₃₋₄₈ tertiary aliphatic amine, C₆₋₃₀ aromatic
30 amine, C₅₋₃₀ heterocyclic amine, or any combination of any of these.

[0066] Exemplified embodiments of the basic compound (D) include ammonia, ethylamine, n-octylamine, n-heptylamine, ethylenediamine, triethylamine, tri-n-octylamine, diethylamine, tris[2-(2-methoxyethoxy)ethyl]amine, 1,8-
35

diazabicyclo[5.4.0]undecene-7, 1,5-
diazabicyclo[4.3.0]nonene-5, 7-methyl-1,5,7-
triazabicyclo[4.4.0]dec-5-ene, 1,5,7-
triazabicyclo[4.4.0]dec-5-ene.

5 [0067] The base dissociation constant $pK_b(H_2O)$ of the basic compound (D) is preferably -12 to 5; more preferably 1 to 4.

[0068] The molecular weight of the basic compound (D) is preferably 17 to 500; more preferably 60 to 400.

10 [0069] The content of the basic compound (D) is preferably 0.01 to 5 mass parts; more preferably 0.05 to 2 mass parts, with respect to 100 mass parts of the polymer (A).

[0070] Surfactant (E)

15 The composition according to the present invention can further contain a surfactant (E). The coatability can be improved by making a surfactant be comprised in it. Examples of the surfactant that can be used in the present invention include (I) anionic surfactants, (II)
20 cationic surfactants or (III) nonionic surfactants, and more particularly (I) alkyl sulfonate, alkyl benzene sulfonic acid and alkyl benzene sulfonate, (II) lauryl pyridinium chloride and lauryl methyl ammonium chloride and (III) polyoxyethylene octyl ether,
25 polyoxyethylene lauryl ether, polyoxyethylene acetylenic glycol ether, fluorine-containing surfactants (for example, Fluorad (3M), Megaface (DIC) and Surflon (AGC)), and organic siloxane surfactants (for example, KF-53 and KP341 (Shin-Etsu Chemical)).

30 [0071] These surfactants can be used alone or in combination of any two or more of these. The content of the surfactant (E) is preferably 0.005 to 1 mass parts; more preferably 0.01 to 0.2 mass parts, with respect to 100 mass parts of the polymer (A).

35 [0072] Dye (F)

The composition according to the present invention

can further contain a dye (F). By including the dye (F), the pattern shape can be improved.

5 The content of the dye (F) is preferably 0 to 0.5 mass parts; more preferably 0 to 0.2 mass parts; further preferably 0 to 0.1 mass parts, with respect to 100 mass parts of the polymer (A). Since the resist film of the present invention preferably has a high transmittance, it is preferred that the resist film does not substantially contain any dye. It is also a more preferred embodiment of the present invention that the composition according to the present invention contains no dye (F) (0 mass parts).

[0073] Additive (G)

15 The composition according to the present invention can further contain an additive (G) other than the above components. The additive (G) is preferably a surface smoothing agent, a plasticizer, a contrast enhancer, an acid, a radical generator, a substrate adhesion enhancer, an antifoaming agent, or any combination of any of these.

20 The content of the additive (G) (in the case of a plurality of additives, the sum thereof) is preferably 0 to 5 mass parts; more preferably 0 to 3 mass parts; further preferably 0 to 1 mass parts, with respect to 100 mass parts of the polymer (A). It is also one embodiment of the present invention that the composition according to the present invention contains no additive (G) (0 mass parts).

30 [0074] The acid can be used to adjust the pH value of the composition and improve the solubility of the additive components. The acid used is not particularly limited, but examples thereof include formic acid, acetic acid, propionic acid, benzoic acid, phthalic acid, salicylic acid, lactic acid, malic acid, citric acid, oxalic acid, malonic acid, succinic acid, fumaric acid, maleic acid, aconitic acid, glutaric acid, adipic acid, and any combination of

any of these.

In the present invention, the content of salicylic acid is preferably 0 to 0.005 mass parts; more preferably 0 to 0.001 mass parts, with respect to 100 mass parts of the polymer (A). It is also one embodiment of the invention that the composition according to the invention contains no salicylic acid (0 mass parts).

[0075] <Method for manufacturing a processed substrate>

The method for manufacturing a processed substrate according to the present invention comprises the following steps:

manufacturing a resist pattern using the composition according to the present invention; and

performing an ion implantation using the resist pattern as a mask, or

processing the underlayer of the resist pattern using the resist pattern as a mask to form a underlayer pattern, and performing an ion implantation using the underlayer pattern as a mask.

[0076] Hereinafter, one embodiment of the manufacturing method according to the present invention is described.

The composition according to the present invention is applied above a substrate (for example, a silicon / silicon dioxide coated substrate, a silicon nitride substrate, a silicon wafer substrate, a glass substrate, an ITO substrate, and the like) by an appropriate method. In the present invention, the "above" includes a case where a layer or film is formed immediately on a substrate and a case where a layer or film is formed above a substrate via another layer. For example, a planarization film or resist underlayer film can be formed immediately on a substrate, and the composition according to the present invention can be applied immediately on the film. The resist underlayer film includes a BARC layer. The application method is not

particularly limited, and examples thereof include a coating method using a spinner or a coater. After application, a film according to the present invention is formed by heating. This heating is performed, for example, by a hot plate. The heating temperature is preferably 100 to 250°C; more preferably 100 to 200°C; further preferably 100 to 160°C. The temperature is a temperature of heating atmosphere, for example, that of a heating surface of a hot plate. The heating time is preferably 30 to 300 seconds; more preferably 30 to 120 seconds; further preferably 45 to 90 seconds. The heating is preferably performed in an air or a nitrogen gas atmosphere.

[0077] The resist film formed by the present invention has high transmittance. The transmittance at a wavelength of 248 nm is preferably 15 to 50%; more preferably 17 to 40%, when the film thickness of the resist film is 5 μm . With these transmittances, the exposure light also reaches the lower portion of the film when the film is thick, and a resist pattern with high rectangularity can be formed.

[0078] The resist film is exposed through a predetermined mask. Although the wavelength of light used for exposure is not particularly limited, it is preferable to perform exposure with light having a wavelength of 13.5 to 248 nm. KrF excimer laser (wavelength: 248 nm), ArF excimer laser (wavelength: 193 nm), extreme ultraviolet (wavelength: 13.5 nm) and the like can be used, and KrF excimer laser is preferred. These wavelengths allow a range of $\pm 1\%$. After exposure, post exposure bake (PEB) can be performed as required. The PEB temperature is preferably 80 to 160°C; more preferably 100 to 150°C, and the heating time is 0.3 to 5 minutes; preferably 0.5 to 2 minutes.

[0079] The exposed resist film is developed using a developer. As the developing method, any method

conventionally used for developing a photoresist, such as a paddle developing method, an immersion developing method, or a swinging immersion developing method, can be used. As the developer, aqueous solution containing an inorganic alkali, such as sodium hydroxide, potassium hydroxide, sodium carbonate and sodium silicate; an organic amine, such as ammonia, ethylamine, propylamine, diethylamine, diethylaminoethanol and triethylamine; a quaternary amine, such as tetramethylammonium hydroxide (TMAH); and the like are used, and a 2.38 mass % TMAH aqueous solution is preferred. A surfactant can also be further added to the developer. The temperature of the developer is preferably 5 to 50°C; more preferably 25 to 40°C, and the development time is preferably 10 to 300 seconds; more preferably 30 to 60 seconds. After development, washing with water or rinsing can also be performed as necessary. When a positive type resist composition is used, the exposed area is removed by development to form a resist pattern. The resist pattern can also be further made finer, for example, using a shrink material.

[0080] When the composition according to the present invention is used, it is possible to form a resist pattern with high resolution, that is, a resist pattern with a high aspect ratio, while it is a thick resist. When the film thickness of the resist film is 3 μm , the resolution is preferably 150 to 220 nm; more preferably 160 to 200 nm.

[0081] When the composition according to the present invention is used, it is possible to form a resist pattern with high rectangularity. When the composition according to the present invention is a positive type resist pattern forming composition, assuming that W_t is the width of the top portion of the resist pattern and W_b is the width of the bottom portion of the resist pattern,

Wt / Wb (hereinafter referred to as Pr) is preferably 0.6 to 1.7; more preferably 0.7 to 1.0; further preferably 0.8 to 1.0.

5 It is preferable to measure by adjusting the conditions for comparing these numerical values as closely as possible to those in Examples described later. For example, it is preferable to compare by forming a film with a film thickness of 3.0 μm , and forming a trench pattern with a line width of 0.8 μm and a space
10 width of 0.2 μm .

[0082] The formed resist pattern has high heat resistance. When the formed trench pattern with a film thickness of 3 μm , a line width of 0.8 μm and a space width of 0.2 μm is heated at 50°C for 60 seconds, the line width
15 variation at the top portion of the pattern before and after heating is preferably 50 nm or less; more preferably 35 nm or less.

[0083] A processed substrate is formed by performing an ion implantation using the resist pattern as a mask, or
20 processing the underlayer of the resist pattern using the resist pattern as a mask to form a underlayer pattern and performing an ion implantation using the underlayer pattern as a mask.

The ion implantation can be performed by a known
25 method using a known ion implantation apparatus. In the manufacture of semiconductor devices, liquid crystal display devices and the like, forming an impurity diffusion layer on a substrate surface is conducted. The formation of an impurity diffusion layer is usually
30 performed in two stages of impurity introduction and diffusion thereof. As one method of the introduction, there is an ion implantation in which impurities such as phosphorus and boron are ionized in a vacuum, accelerated in a high electric field and implanted into
35 the support surface. As the ion acceleration energy during ion implantation, an energy load of 10 to 200 keV

is generally applied to the resist pattern, which can destroy the resist pattern.

5 Since the resist pattern formed according to the present invention is a thick film, has high rectangularity, and has high heat resistance, it can be suitably used for ion implantation applications in which ions are implanted at high energy.

10 Ion sources (impurity elements) include ions such as boron, phosphorus, arsenic and argon. Thin films on substrates include silicon, silicon dioxide, silicon nitride, aluminum and the like.

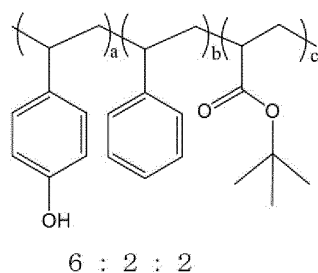
[0084] Thereafter, if necessary, further processing such as forming wiring on the processed substrate is performed to form a device. For these further processing, known methods can be applied. Examples of the device include a semiconductor device, a liquid crystal display device, an organic EL display device, a plasma display device, and a solar cell device. The device is preferably a semiconductor device.

20 [Examples]

[0085] The present invention is described below with reference to various examples. The embodiment of the present invention is not limited only to these examples.

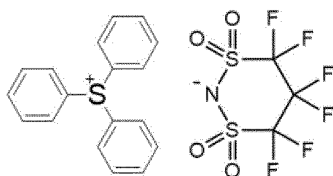
[0086] Preparation of Composition 1

25 100 mass parts of polymer 1, 1.00 mass part of photoacid generator 1, 0.15 mass parts of basic compound 1, and 0.06 mass parts of surfactant 1 are added to a mixed solvent having a mass ratio of PGME : EL = 70 : 30, so that the solid content ratio becomes 30 25.0 mass %. The resultant is stirred for 30 minutes at room temperature. It is visually checked that the added materials are dissolved. The resultant is filtered through a 0.05 μm filter. Thereby, Composition 1 is obtained.



(Polymer 1) Hydroxystyrene : styrene : t-butyl acrylate copolymer, molar ratio 6 : 2 : 2, Mw: about 9,000

The above ratio indicates the ratio of the number of structural units of each repeating unit, and the same applies hereinafter.



(Photoacid generator 1)

Basic compound 1: tris[2-(2-methoxyethoxy)-ethyl]amine

Surfactant 1: Megaface R-40, DIC Corporation

[0087] Preparation of Compositions 2 to 11 and Comparative Composition 1

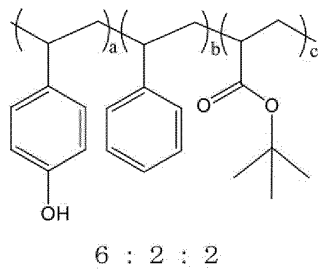
The constituent is changed as shown in Table 1, the solvent is the same as Composition 1, and the solid content ratio is the same as Composition 1, and the preparation is performed in the same manner as Composition 1 to obtain Compositions 2 to 11 and Comparative Composition 1. In the table, the numerical values of each constituent indicate mass parts.

[Table 1]

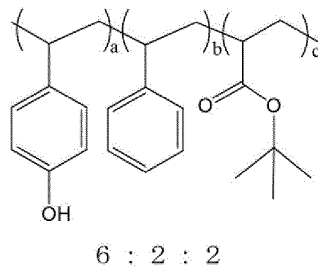
Table 1

	Composition											Compa rative compo sition
	1	2	3	4	5	6	7	8	9	10	11	1
Polymer 1	100	—	—	—	—	—	—	—	—	—	—	—
Polymer 2	—	100	—	—	100	100	—	—	—	100	99.5	—
Polymer 3	—	—	100	—	—	—	—	—	—	—	—	—
Polymer 4	—	—	—	100	—	—	—	—	—	—	—	—
Polymer 5	—	—	—	—	—	—	—	—	—	—	—	100
Polymer 6	—	—	—	—	—	—	100	—	—	—	—	—
Polymer 7	—	—	—	—	—	—	—	100	—	—	—	—
Polymer 8	—	—	—	—	—	—	—	—	100	—	—	—
Polymer 9	—	—	—	—	—	—	—	—	—	—	0.5	—
Photoacid generator 1	1	1	1	1	0.5	2	1	1	1	—	1	1
Photoacid generator 2	—	—	—	—	—	—	—	—	—	1	—	—
Basic compound1	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Surfactant 1	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06

In the table,
•Polymer 2

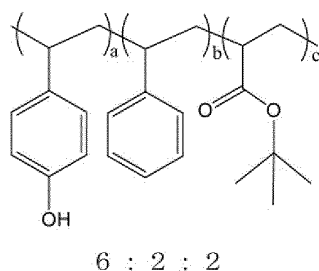


- 5
- Hydroxystyrene : styrene : t -butyl acrylate copolymer,
molar ratio 6 : 2 : 2 , Mw: about 12,000
•Polymer 3



- 10
- Hydroxystyrene : styrene : t-butyl acrylate copolymer,
molar ratio 6 : 2 : 2 , Mw: about 15,000

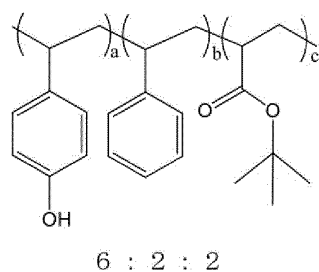
•Polymer 4



Hydroxystyrene : styrene : t-butyl acrylate copolymer,
molar ratio 6 : 2 : 2, Mw: about 18,000

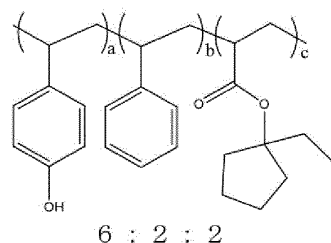
5

•Polymer 5 (comparative polymer)



Hydroxystyrene : styrene : t-butyl acrylate copolymer,
molar ratio 6 : 2 : 2, Mw: about 24,000

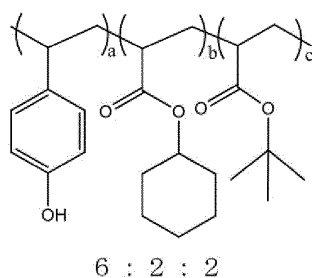
•Polymer 6



10

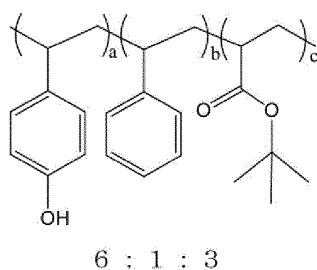
Hydroxystyrene : styrene : ethylcyclopentyl acrylate
copolymer, molar ratio 6 : 2 : 2, Mw: about 12,000

•Polymer 7



Hydroxystyrene : cyclohexyl acrylate : t-butyl acrylate
copolymer, molar ratio 6 : 2 : 2, Mw: about 12,000

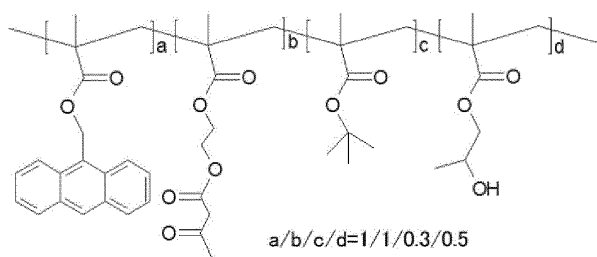
•Polymer 8



5

Hydroxystyrene : styrene : t-butyl acrylate copolymer,
molar ratio 6 : 1 : 3, Mw: about 12,000

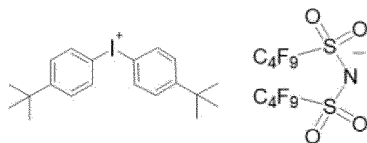
•Polymer 9



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Anthracenemethanol methacrylate : acetoacetoxyethyl
methacrylate : 2-hydroxypropyl methacrylate : t-butyl
methacrylate copolymer, molar ratio 1 : 1 : 0.3 : 0.5,
Mw: about 15,000

•Photoacid generator 2



[0088] Example of resist pattern formation

Using a coater developer Mark 8 (Tokyo Electron), the composition prepared above is dropped onto an 8 inch Si wafer and spin-coating is performed. This wafer is heated at 140°C for 90 seconds using a hot plate under atmospheric conditions to form a resist film. The thickness of the resist film at this point is 3.0 μm when measured by an optical interference type film thickness measuring device M-1210 (SCREEN).

This resist film is exposed using a KrF stepper FPA3000-EX5 (Canon). The exposed wafer is heated (PEB) at 120°C for 90 seconds using a hot plate under atmospheric conditions. Thereafter, this resist film is puddle-developed with a 2.38 mass % TMAH aqueous solution for 60 seconds, washed with DIW, and spin-dried at 1,000 rpm. Thereby, a trench pattern with a line width of 0.8 μm and a space width of 0.2 μm is formed. The line width and space width are values measured at the bottom portion of the pattern.

Figure 1 schematically shows a vertical cross-sectional shape of this pattern. A trench pattern 2 is formed on a substrate 1. The exposure dose for forming a trench pattern having a line width of 0.8 μm and a space width of 0.2 μm is taken as the optimum exposure dose, and the resolution described later is evaluated at this optimum exposure dose.

[0089] Evaluation of pattern rectangularity

A section of the sample formed in the above-described "Example of resist pattern formation" is formed and the vertical cross section of the pattern is observed with a scanning type electron microscope (SEM). The ratio of the width of the top portion of the

pattern to the width of the bottom portion of the pattern is evaluated. Figure 2 schematically shows a vertical cross section, in which a trench pattern 2 is formed on a substrate 1. It is assumed that W_t is the width of the top portion of the pattern, and W_b is the width of the bottom portion of the pattern. This ratio Pr is defined as $Pr = W_t / W_b$ and used as an index for the rectangularity evaluation of the pattern.

The evaluation criteria are as follows:

A: Pr is 0.8 to 1.0.

B: Pr is 0.7 to 0.8.

C: Pr is 1.0 or more, or 0.7 or less.

The evaluation results are described in Table 2.

[0090] Evaluation of resolution

Using a mask pattern with a space size of 0.25 to 0.16 μm , exposure is performed with the optimum exposure dose by the pattern forming method described above. The resolution is taken as the minimum dimension (μm) of the resist pattern that is resolved when exposed with the optimum exposure dose. For those that cannot form a pattern of 0.20 μm , the minimum size that can be formed is taken as the resolution.

The evaluation results are described in Table 2.

[0091] Evaluation of transmittance

Each composition is dropped onto a quartz substrate and spin-coating is performed. This wafer is heated at 140°C for 90 seconds using a hot plate under atmospheric conditions to form a resist film having a film thickness of 5.0 μm . The transmission spectrum of this film is measured using an ultraviolet-visible spectrometer (Thermo Fisher Scientific). The transmittance at 248 nm at this time is taken as the transmittance for evaluation. The reference is a quartz substrate on which no resist film is formed.

[0092] Evaluation of heat resistance

The substrate patterned in the above-described "Example of resist pattern formation" is heated at 150°C for 60 seconds using a hot plate. After that, a change in pattern shape is observed using an SEM from a vertical cross section. The evaluation criteria are as follows:

A: No change in shape is observed

B: There is a change at the top portion of the resist pattern, and the amount of deformation is 50 nm or less.

C: The amount of deformation at the top portion of the resist pattern is larger than 50 nm.

[Table 2]

	Pr	Evaluation of rectangularity	Resolution	Evaluation of resolution	Transmittance %T	Heat resistance deformation amount	Evaluation of heat resistance
Composition 1	0.77	B	185nm	A	23	20nm	B
Composition 2	0.82	A	190nm	A	23	0nm	A
Composition 3	0.84	A	195nm	B	23	0nm	A
Composition 4	0.82	A	200nm	B	23.5	0nm	A
Composition 5	0.95	A	200nm	B	27	0nm	A
Composition 6	0.71	B	180nm	A	19	0nm	A
Composition 7	0.89	A	180nm	A	23	0nm	A
Composition 8	0.86	A	200nm	B	26	30nm	B
Composition 9	0.77	B	200nm	B	23	10nm	A
Composition 10	0.85	A	170nm	A	23	0nm	A
Comparative composition 1	0.51	C	205nm	C	24	0nm	A

15 [0093] Evaluation of Composition 11

The following evaluations are performed using Composition 11.

When the resolution is evaluated in the same manner as above, the resolution is 180 nm, which is rated an A. When the heat resistance is evaluated in the same manner as above, the amount of deformation is 0 nm, which is rated an A.

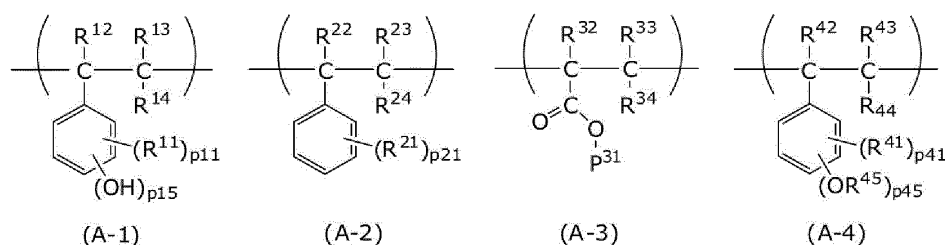
[Explanation of symbols]

[0094] 1. substrate

2. trench pattern

Patent Claims

1. An ion implantation thick film resist composition comprising a polymer (A), a photoacid generator (B) and a solvent (C),
wherein,
the film thickness of the resist film formed from the composition is 1.0 to 50 μm ;
the mass average molecular weight of the polymer (A) is 5,000 to 19,000; and
the polymer (A) comprises at least one of the repeating unit represented by formulae (A-1), (A-2), (A-3) and (A-4):



wherein

- R¹¹, R²¹, R⁴¹ and R⁴⁵ are each independently C₁₋₅ alkyl (wherein methylene in the alkyl can be replaced with oxy);
R¹², R¹³, R¹⁴, R²², R²³, R²⁴, R³², R³³, R³⁴, R⁴², R⁴³ and R⁴⁴ are each independently hydrogen, C₁₋₅ alkyl, C₁₋₅ alkoxy or -COOH;
p₁₁ is 0 to 4, p₁₅ is 1 to 2, and p₁₁ + p₁₅ ≤ 5;
p₂₁ is 0 to 5;
p₄₁ is 0 to 4, p₄₅ is 1 to 2, and p₄₁ + p₄₅ ≤ 5;
P³¹ is C₄₋₂₀ alkyl (wherein a part or all of the alkyl can form a ring, a part or all of H in the alkyl can be replaced with halogen, and methylene in the alkyl can be replaced with oxy or carbonyl).

2. The composition according to claim 1, wherein the transmittance at a wavelength of 248 nm is 15 to 50% when the film thickness of the resist film is 5 μm .

3. The composition according to claim 1 or 2, wherein n_{A-1} , n_{A-2} , n_{A-3} and n_{A-4} , which are the numbers of repeating units represented by formulae (A-1), (A-2), (A-3) and (A-4) in the polymer (A) satisfy the following:

$$n_{A-1} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 40 \text{ to } 80\%,$$

$$n_{A-2} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0 \text{ to } 40\%,$$

$$n_{A-3} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 10 \text{ to } 50\%, \text{ or}$$

$$n_{A-4} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0 \text{ to } 40\%:$$

preferably, n_{total} , which is the number of all repeating units contained in the polymer (A), satisfies the following:

$$(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) / n_{total} = 80 \text{ to } 100\%.$$

4. The composition according to one or more of claims 1 to 3, wherein the resolution is 150 to 220 nm when the film thickness of the resist film is 3 μm .

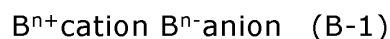
5. The composition according to one or more of claims 1 to 4, wherein,

when a trench pattern having a film thickness of 3 μm , a line width of 0.8 μm and a space width of 0.2 μm formed from the resist film is heated at 50°C for 60 seconds, the line width variation at the top portion of the pattern before and after heating is 50 nm or less, and

in the trench pattern, the width W_t of the top portion of the pattern and the width W_b of the bottom portion of the pattern satisfy the following:

$$0.6 \leq W_t / W_b \leq 1.7$$

6. The composition according to one or more of claims 1 to 5, wherein the photoacid generator (B) is represented by the formula (B-1):

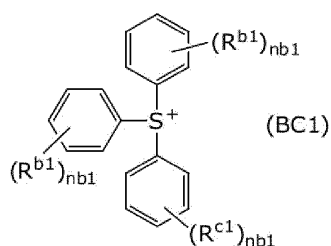


wherein

the $B^{n+}\text{cation}$ is a cation represented by the formula (BC1), a cation represented by the formula (BC2) or a cation represented by the formula (BC3), the $B^{n+}\text{cation}$ is n valent as a

whole, and n is 1 to 3, and

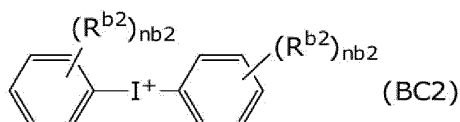
the B^{n-} anion is an anion represented by the formula (BA1), an anion represented by the formula (BA2), an anion represented by the formula (BA3) or an anion represented by the formula (BA4), and the B^{n-} anion is n valent as a whole:



wherein

R^{b1} is each independently C_{1-6} alkyl, C_{1-6} alkoxy, C_{6-12} aryl, C_{6-12} arylthio or C_{6-12} aryloxy, and

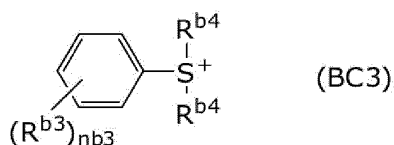
$nb1$ is each independently 0, 1, 2 or 3;



wherein

R^{b2} is each independently C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl, and

$nb2$ is each independently 0, 1, 2 or 3;

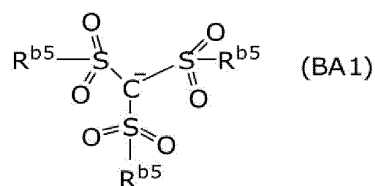


wherein

R^{b3} is each independently hydroxy, C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl,

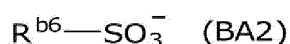
R^{b4} is each independently C_{1-6} alkyl, provided that two R^{b4} can be bonded to each other to form a ring structure, and

$nb3$ is each independently 0, 1, 2 or 3;



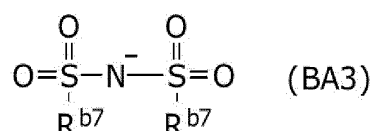
wherein

R^{b5} is each independently fluorine-substituted C_{1-6} alkyl, fluorine-substituted C_{1-6} alkoxy, or C_{1-6} alkyl;



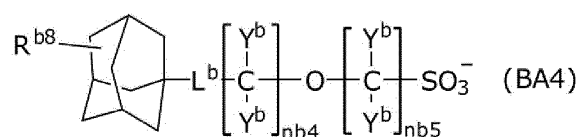
wherein

R^{b6} is fluorine-substituted C_{1-10} alkyl, fluorine-substituted C_{1-6} alkoxy, fluorine-substituted C_{6-12} aryl, fluorine-substituted C_{2-12} acyl or fluorine-substituted C_{6-12} alkoxyaryl;



wherein

R^{b7} is each independently fluorine-substituted C_{1-6} alkyl, fluorine-substituted C_{1-6} alkoxy, fluorine-substituted C_{6-12} aryl, fluorine-substituted C_{2-12} acyl or fluorine-substituted C_{6-12} alkoxyaryl, wherein two R^{b9} can be bonded to each other to form a fluorine-substituted heterocyclic structure;



wherein

R^{b8} is hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy or hydroxy,
 L^{b2} is methylene, ethylene, carbonyl, oxy or carbonyloxy,
 Y^{b} is each independently hydrogen or fluorine,
 nb4 is an integer of 0 to 10, and
 nb5 is an integer of 0 to 21.

7. The composition according to one or more of claims 1 to 6, wherein the solvent (C) is propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, ethyl lactate, n-butyl acetate, n-butyl ether, 2-heptanone, cyclohexanone, or any combination of any of these.
8. The composition according to one or more of claims 1 to 7, further comprising a basic compound (D):
preferably, the basic compound (D) is ammonia, C₁₋₁₆ primary aliphatic amine, C₂₋₃₂ secondary aliphatic amine, C₃₋₄₈ tertiary aliphatic amine, C₆₋₃₀ aromatic amine, C₅₋₃₀ heterocyclic amine, or any combination of any of these; or
preferably, the content of the basic compound (D) is 0.01 to 5 mass parts with respect to 100 mass parts of the polymer (A).
9. The composition according to one or more of claims 1 to 8, further comprising a surfactant (E):
preferably, the content of the surfactant (E) is 0.005 to 1 mass parts with respect to 100 mass parts of the polymer (A).
10. The composition according to one or more of claims 1 to 9, further comprising a dye (F):
preferably, the content of the dye (F) is 0 to 0.5 mass parts with respect to 100 parts mass parts of the polymer (A).
11. The composition according to one or more of claims 1 to 10, further comprising an additive (G):
preferably, the additive (G) is a surface smoothing agent, a plasticizer, a contrast enhancer, an acid, a radical generator, a substrate adhesion enhancer, an antifoaming agent, or any combination of any of these; or
preferably the content of the additive (G) is 0 to 5 mass parts with respect to 100 mass parts of the polymer (A).
12. The composition according to one or more of claims 1 to

11, wherein the polymer (A) contains a further repeating unit other than the repeating units represented by the formulae (A-1) to (A-4):

preferably, the content of the further repeating unit contained in the polymer (A) is 0 to 10 mass parts with respect to 100 mass parts of the polymer (A); or

preferably, the further repeating unit comprises arylcarbonyl.

13. The composition according to one or more of claims 1 to 12, wherein the content of salicylic acid is 0 to 0.005 mass parts with respect to 100 mass parts of the polymer (A).

14. The composition according to one or more of claims 1 to 13, wherein
the content of the polymer (A) is 10 to 40 mass % based on the composition,
the content of the photoacid generator (B) is 0.3 to 4 mass parts, preferably 0.4 to 2 mass parts, with respect to 100 mass parts of the polymer (A), and
the content of the solvent (C) is 50 to 90 mass % based on the composition.

15. A method for manufacturing a processed substrate, comprising the following steps:
manufacturing a resist pattern using the composition according to one or more of claims 1 to 14; and
performing an ion implantation using the resist pattern as a mask, or
processing the underlayer of the resist pattern using the resist pattern as a mask to form a underlayer pattern, and performing an ion implantation using the underlayer pattern as a mask.

16. A method for manufacturing a device comprising the method according to claim 15:
preferably, further comprising forming wiring on the processed substrate.