

THICK FILM CHEMICALLY AMPLIFIED POSITIVE TYPE RESIST
COMPOSITION AND METHOD FOR MANUFACTURING RESIST FILM USING
THE SAME

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001]

The present invention relates to a thick film chemically amplified positive type resist composition to be used in manufacturing semiconductor devices, semiconductor integrated circuits and the like, and a method for manufacturing a resist film using the same.

BACKGROUND ART

[0002]

In a process of manufacturing devices such as semiconductor, fine processing by lithographic technique using a resist has generally been employed. The fine processing process comprises forming a thin resist layer on a semiconductor substrate such as a silicon wafer, covering the layer with a mask pattern corresponding to a desired device pattern, exposing the layer with actinic ray such as ultraviolet ray through the mask, developing the exposed layer to obtain a resist pattern, and etching the substrate using the resulting resist pattern as a protective film, thereby forming fine unevenness corresponding to the above-described pattern.

[0003]

While requiring making the resist pattern finer, there is a demand for a resist pattern that is thicker and has a higher aspect ratio in order to cope with high-energy ion implantation and the like. When forming a thick film resist pattern, unlike the case of a thin film, the performance and process conditions required for the composition are different. Therefore, there are characteristic difficulties that the required shape cannot be formed only by adjusting the viscosity of the thin film resist composition to make it thicker.

[0004]

Patent Document 1 studies a positive type resist composition for forming a thick film resist using a mixed solvent containing propylene glycol monomethyl ether (PGME). As a solvent to be combined with PGME, a high boiling point solvent is considered to be preferable, but a resist film having a film thickness of 11 μm or more has not been studied.

Patent Document 2 studies a resist composition for forming a thick

film resist containing a solvent having a certain viscosity and a saturated vapor pressure for the purpose of improving liquid feeding properties, but a resist film having a film thickness of 11 μm or more has not been studied.

Patent Document 3 studies forming a resist film having a film thickness of 7 μm or more using a certain resin.

Patent Document 4 studies a resist for forming a thick film using a certain acid generator, but a resist film having a film thickness of 11 μm or more has not been studied.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0005]

[Patent document 1] JP 2007-248727 A

[Patent document 2] JP 2016-206673 A

[Patent document 3] JP 2019-120765 A

[Patent document 4] JP 2007-206425 A

SUMMARY OF THE INVENTION

[0006]

The present inventors considered that there are one or more problems still need improvement in thick film chemically amplified positive type resist compositions and use thereof. These include, for example, the followings:

When the film thickness is increased, a scooped-out area part on the top of a resist pattern wall is more pronounced. The number of defects is large. Cracks are generated in the resist pattern. Resistance to the process after development is low. The resist film or resist pattern is easily affected by heat.

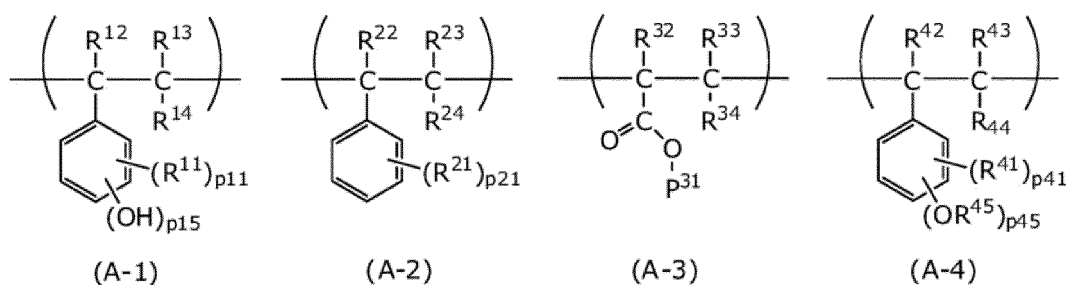
[0007]

A thick film chemically amplified positive type resist composition according to the present invention contains an alkali-soluble resin (A), a photoacid generator (B) and a solvent (C),

wherein,

the film thickness of the resist film formed from the thick film chemically amplified positive type resist composition is 11.0 to 50.0 μm ;

the alkali-soluble resin (A) comprises at least one of the following repeating units:



(where,

R^{11} , R^{21} , R^{41} and R^{45} are each independently C_{1-5} alkyl (in which - CH_2 - in the alkyl can be replaced with -O-);

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 (in which all or part of the alkyl can form a ring, and all or part of H in the alkyl can be substituted with halogen)); and

the solvent (C) comprises propylene glycol monomethyl ether (PGME) (C-1), and the content of PGME (C-1) is more than 50 mass % and 100 mass % or less, based on the solvent (C).

[0008]

A method for manufacturing a resist film according to the present invention includes steps below:

(1) applying the above-described composition above a substrate; and

(2) heating the composition to form a resist film.

[0009]

Using the thick film chemically amplified positive type resist composition according to the present invention, it is possible to desire one or more of the following effects.

In a resist film having a very large film thickness, a resist pattern good in shape can be formed. The scooped-out area on the top of the resist pattern wall can be suppressed. The number of defects can be reduced. In the process after development (for example, etching), a resist pattern with sufficient resistance can be obtained. Favorable sensitivity can be obtained even with a resist film of thick film. Heat resistance of the resist film or resist pattern is sufficient. Cracks can be suppressed with a resist film of thick film.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIGS. 1A and 1B are schematic views showing the cross-sectional shape of a resist pattern; and

FIG. 2 is a schematic view showing the top of a resist pattern wall.

DETAILED DESCRIPTION OF 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.

"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% 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 (methyl, ethyl, propyl, butyl, pentyl, hexyl etc.).

When a polymer has a plural types of repeating units, these repeating units copolymerize. These copolymerization are any of alternating 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 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 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.

[0012]

Hereinafter, embodiments of the present invention are described in detail.

[0013]

Thick film chemically amplified positive type resist composition

The thick film chemically amplified positive type resist composition according to the present invention (hereinafter referred to as the composition) contains an alkali-soluble resin (A), a photoacid generator (B), and a solvent (C).

The thick film resist composition means a resist composition capable of forming a resist film of thick film. In the present invention, the film thickness of the resist film formed from the thick film resist composition is 11.0 to 50 μm (preferably 11.0 to 20 μm ; more preferably 11.0 to 18 μm ; further preferably 12 to 18 μm).

The solid component concentration of the composition according to the present invention is preferably more than 0 mass % and less than 80 mass %, more preferably 30 to 50 mass %, and more preferably 35 to 45 mass %. The solid component concentration is the concentration of all other components except the solvent based on the composition.

The viscosity is preferably 100 to 3,000 cP, more preferably 150 to 2,500 cP, and further preferably 200 to 2,000 cP. The viscosity is measured at 25°C with a capillary viscometer.

The composition according to the present invention is preferably a thick film chemically amplified positive type KrF resist composition. Here, the term KrF used in the above preferred examples means that a KrF excimer laser is used when exposing a resist film formed from a resist composition.

[0014]

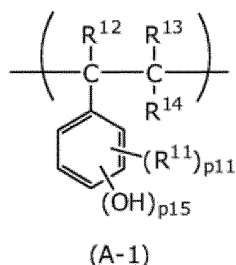
(A) Alkali-soluble resin

The composition according to the present invention comprises an alkali-soluble resin (A) (hereinafter referred to as the component (A); the same applies to other components). The component (A) comprises at least one of repeating units represented by the following formulas (A-1), (A-2), (A-3) and (A-4). The component (A) is that reacts with an acid to increase its solubility in an alkaline aqueous solution. Such an alkali-soluble resin is that has, for example, an acid group protected by a protecting group, and when an acid is added from the outside, the protecting group is eliminated and the solubility in an alkaline aqueous

solution is increased. Such a component (A) can be freely selected from those commonly used in lithography methods.

[0015]

The formula (A-1) is as follows:



where,

R^{11} is each independently C_{1-5} alkyl (in which 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 with 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., it is not intended to have alkoxy or hydroxy.

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

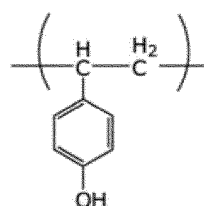
p_{11} is 0 to 4; preferably 0 or 1; more preferably 0.

p_{15} is 1 to 2; preferably 1.

$p_{11} + p_{15} \leq 5$ is satisfied.

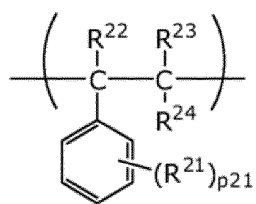
[0016]

Exemplified embodiments of the formula (A-1) include the followings.



[0017]

The formula (A-2) is as follows:



(A-2)

where,

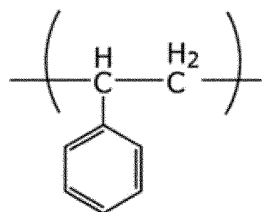
R^{21} is each independently C_{1-5} alkyl (in which methylene in the alkyl may be replaced with oxy); preferably methyl, ethyl, t-butyl or t-butoxy; more preferably methyl or ethyl; further preferably methyl.

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

$p21$ is 0 to 5; preferably 0, 1, 2, 3, 4 or 5; more preferably 0 or 1; further preferably 0.

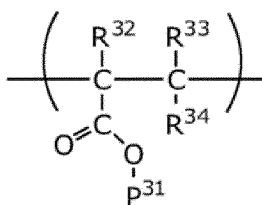
[0018]

Exemplified embodiments of the formula (A-2) include the followings.



[0019]

The formula (A-3) is as follows:



(A-3)

where

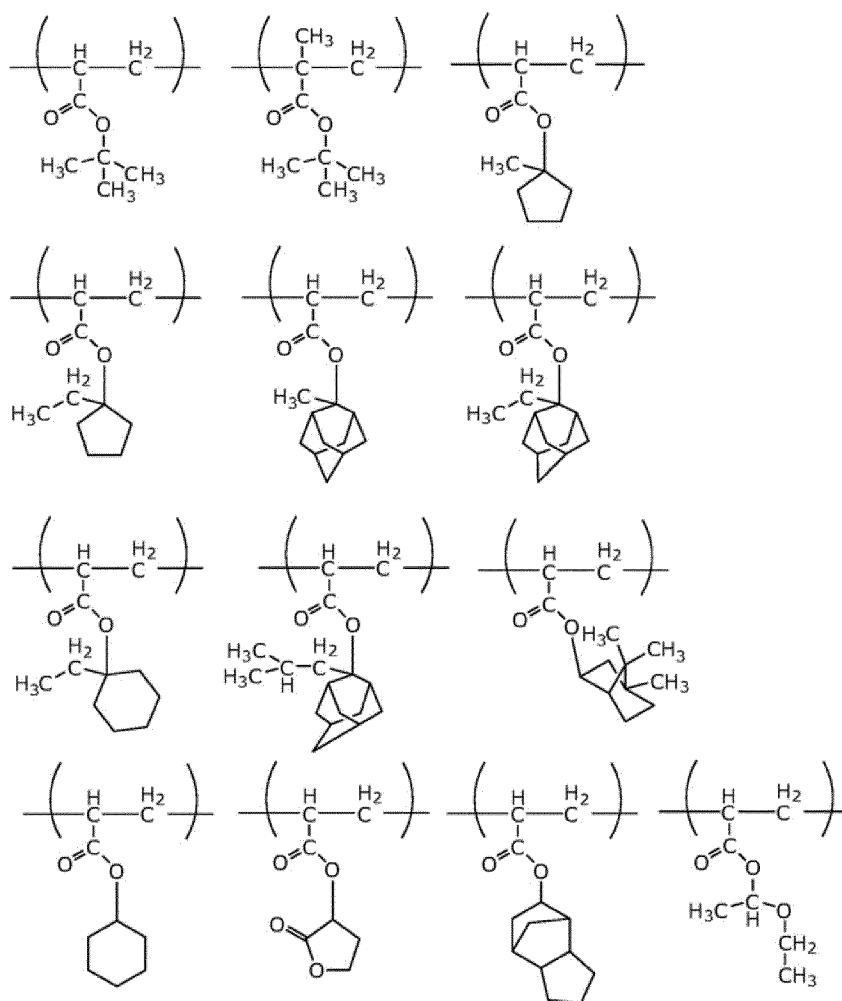
R^{32} , R^{33} , and R^{34} are each independently hydrogen, C_{1-5} alkyl, C_{1-5}

alkoxy or -COOH; preferably hydrogen, methyl, ethyl, t-butyl, methoxy, t-butoxy or -COOH; more preferably hydrogen or methyl; further preferably hydrogen.

P³¹ is C₄₋₂₀ alkyl. Some or all of alkyl can form a ring, some or all of H of the alkyl can be substituted with halogen, and methylene in the alkyl can be replaced with oxy or carbonyl. The alkyl moiety of P³¹ is preferably branched or cyclic. When the C₄₋₂₀ alkyl in P³¹ is substituted 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 C₄₋₂₀ alkyl in P³¹ is not replaced with any halogen. P³¹ 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.

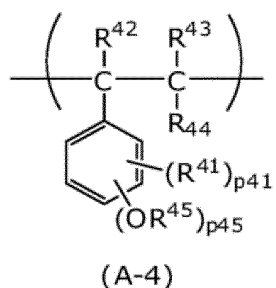
[0020]

Exemplified embodiments of the formula (A-3) include the followings.



[0021]

The formula (A-4) is as follows:



where

R^{41} is each independently C_{1-5} alkyl (in which methylene in the alkyl can be replaced with oxy); preferably methyl, ethyl or t-butyl; more preferably methyl.

R^{45} is each independently C_{1-5} alkyl (in which methylene in the alkyl can be replaced with oxy); preferably methyl, t-butyl or $-CH(CH_3)-O-CH_2CH_3$.

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

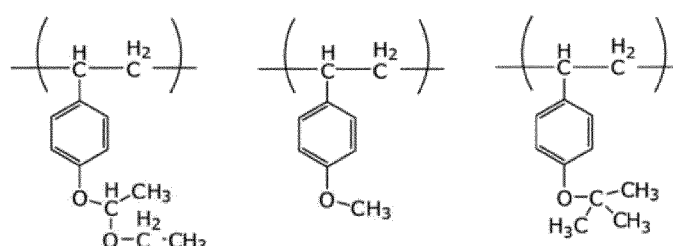
p41 is 0 to 4; more preferably 0 or 1; further preferably 0.

p45 is 1 to 2; more preferably 1.

$p41 + p45 \leq 5$ is satisfied.

[0022]

Exemplified embodiments of the formula (A-4) include the followings.



[0023]

The alkali-soluble resin (A) can comprise plural kinds of repeating units represented by the formula (A-1), (A-2), (A-3) or (A-4). For example, it is possible for the alkali-soluble resin (A) 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.

In a preferred embodiment of the present invention, the alkali-soluble resin (A) comprises two or more kinds of repeating units represented by the formula (A-3), more preferably comprises two kinds of repeating units represented by the formula (A-3).

[0024]

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

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 alkali-soluble resin (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 45 to 75%, further preferably 50 to 70%; and 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 35%; further preferably 5 to 35%; and further more preferably 15 to 25%.

$n_{A-3}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0 to 40%; more preferably 10 to 40%; further preferably 15 to 30%; and 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%; and further more preferably 0 to 5%. It is also a preferred embodiment of the present invention that n_{A-4} is 0.

As an embodiment of the present invention, $n_{A-3} > 0$ and $n_{A-4} = 0$.
[0025]

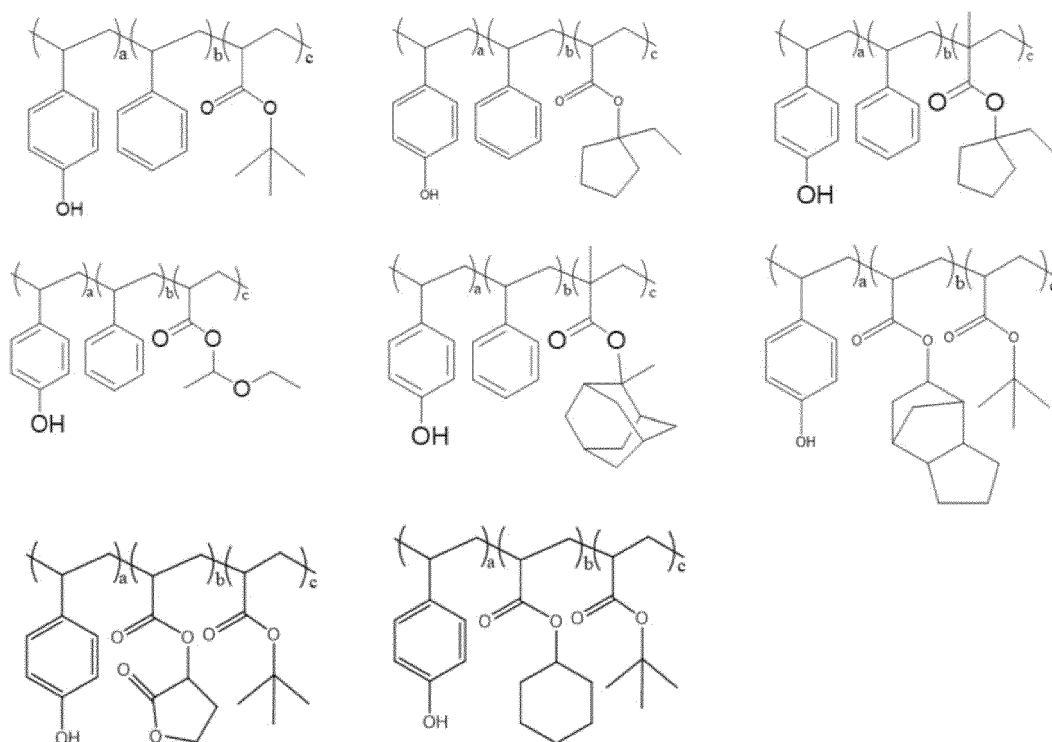
The alkali-soluble resin (A) can also comprise additional repeating units other than the repeating units represented by the formulae (A-1), (A-2), (A-3) and (A-4).

n_{total} , which is the total number of all repeating units included in the alkali-soluble resin (A), satisfies the following:

$(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})/n_{total} =$ preferably 80 to 100%, more preferably 90 to 100%, and further preferably 95 to 100%. It is also a preferred embodiment of the alkali-soluble resin (A) to include no further repeating unit.

[0026]

Exemplified embodiments of the alkali-soluble resin (A) includes the following:



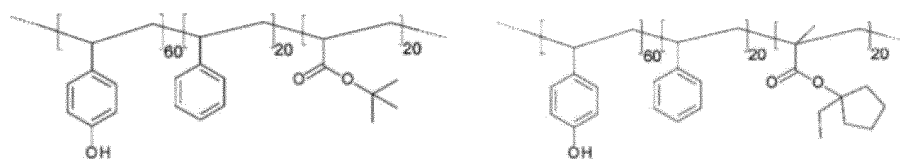
[0027]

The mass average molecular weight (hereinafter referred to as Mw in some cases) of the alkali-soluble resin (A) is 12,000 to 50,000; more preferably 12,000 to 40,000; further preferably 12,000 to 30,000; and further more preferably 15,000 to 30,000. Without wishing to be bound by theory, it is considered that due to the alkali-soluble resin (A) having this Mw, it becomes possible to suppress cracks when a resist pattern is formed 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]

Description will be made for the sake of explanation. In the composition according to the present invention, as long as the alkali-soluble resin (A) is represented by the above formula, two or more kinds thereof can also be used in combination. For example, a composition containing both of the following two alkali-soluble resins (A) is also an embodiment of the present invention.



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

The component (A) consists of one or two kinds of polymers, preferably one kind of polymer. Variation in Mw distribution and polymerization is acceptable.

[0029]

The content of the component (A) is preferably more than 0 mass % and 50 mass % or less, 15 to 50 mass %, more preferably 20 to 45 mass %, further preferably 30 to 40 mass %, based on the composition.

[0030]

(B) Photoacid generator

The composition according to the present invention contains a photoacid generator (B). The component (B) releases an acid by light irradiation. Preferably, an acid derived from the component (B) acts on the component (A) to play a role of increasing the solubility of the component (A) in an alkaline aqueous solution. For example, when the component (A) has an acid group protected by a protecting group, the protecting group is made eliminated by the acid. The component (B) used in the composition according to the present invention can be selected from conventionally known ones.

[0031]

By exposure, the component (B) releases an acid having an acid dissociation constant pK_a (H_2O) of preferably -20 to 1.4; more preferably -16 to 1.4; further preferably -16 to 1.2; further more preferably -16 to 1.1.

[0032]

The component (B) is preferably represented by the formula (B-1) or the formula (B-2).

[0033]

The formula (B-1) is as follows:

B^{n+} cation B^{n-} anion (B-1)

where,

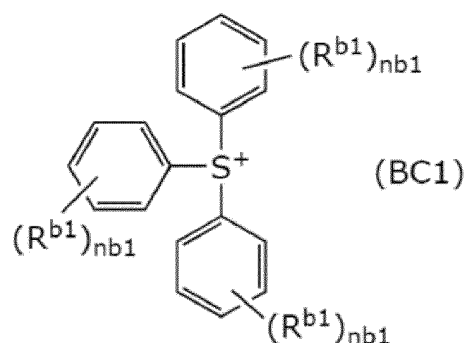
B^{n+} cation is a cation represented by the formula (BC1), a cation

represented by the formula (BC2), or a cation represented by the formula (BC3), B^{n+} cation is n valent as a whole, and n is 1 to 3, preferably 1 or 2, more preferably 1, and

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 B^{n-} anion is n valent as a whole.

[0034]

The formula (BC1) is as follows:



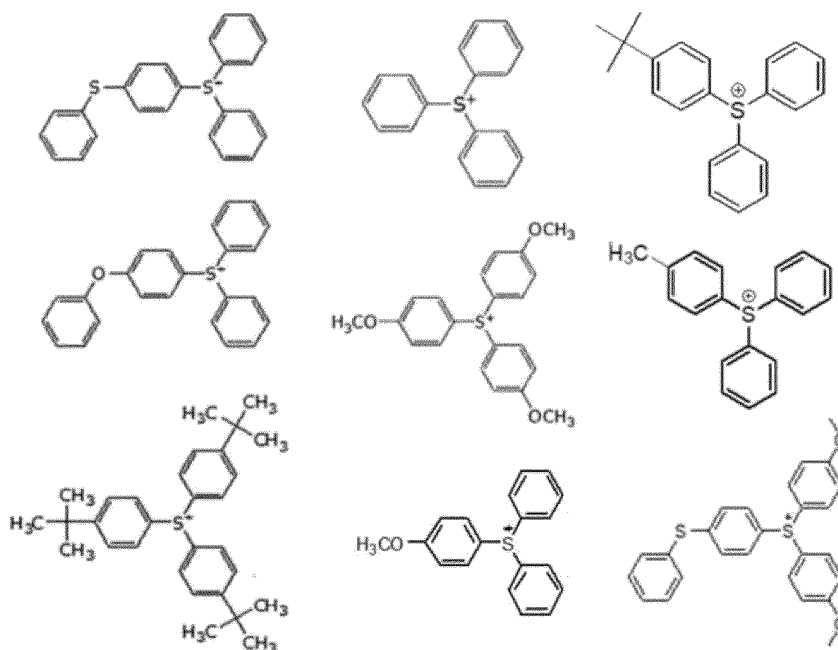
where,

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. It is also a preferred embodiment that all $nb1$ are 1 and all R^{b1} are identical. It is also a preferred embodiment that $nb1$ is 0.

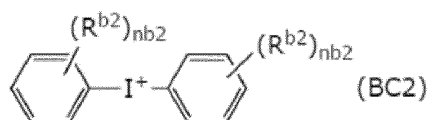
[0035]

Exemplified embodiments of the formula (BC1) are as follows.



[0036]

The formula (BC2) is as follows:



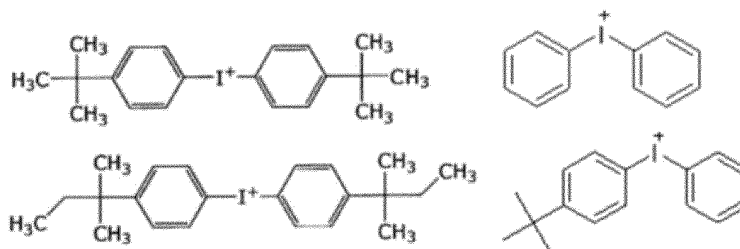
where,

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, more preferably t-butyl or 1,1-dimethylpropyl, further more preferably t-butyl.

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

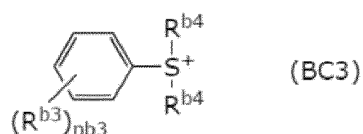
[0037]

Exemplified embodiments of the formula (BC2) are as follows.



[0038]

The formula (BC3) is as follows:



where,

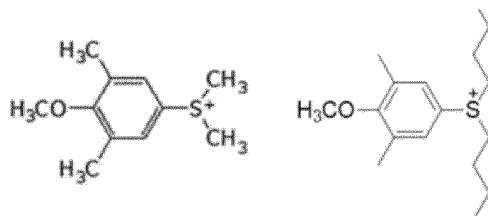
R^{b3} is each independently C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl, preferably methyl, ethyl, methoxy or ethoxy, more preferably methyl or methoxy.

R^{b4} is each independently C_{1-6} alkyl, preferably methyl or ethyl, more preferably methyl.

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

[0039]

An exemplified embodiment of the formula (BC3) is as follows.

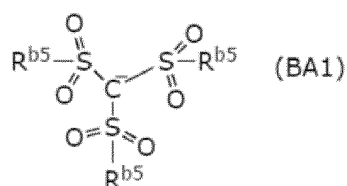


[0040]

The B^{n+} cation selected from the group consisting of the cations represented by the formula (BC1) or (BC2) is preferable because it exhibits a better effect.

[0041]

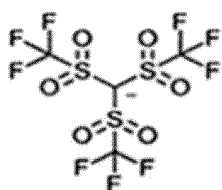
The formula (BA1) is as follows:



R^{b5} is each independently C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, or C_{1-6} alkyl. For example, $-CF_3$ means that all of the hydrogen of methyl (C_1) are substituted with fluorine. Preferably all of the hydrogen present in the C_{1-6} fluorine-substituted alkyl is substituted with fluorine. The alkyl moiety of R^{b5} is preferably methyl, ethyl, or t-butyl (more preferably methyl). In a preferred embodiment, R^{b5} is preferably a fluorine-substituted alkyl, more preferably $-CF_3$.

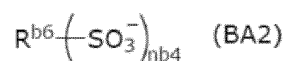
[0042]

An exemplified embodiment of the formula (BA1) is as follows.



[0043]

The formula (BA2) is as follows:



where,

R^{b6} is C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl or C_{6-12} fluorine-substituted alkoxyaryl, preferably C_{2-6} fluorine-substituted alkyl, more preferably C_{2-3} fluorine-substituted alkyl, further preferably C_3 fluorine-substituted alkyl. In the fluorine-substituted alkyl of R^{b6} , an embodiment in which all the hydrogen present in the alkyl moiety are substituted with fluorine is preferable. The alkyl moiety of R^{b6} is preferably methyl, ethyl, propyl, butyl or pentyl, more preferably propyl, butyl or pentyl; further preferably butyl. The alkyl moiety of R^{b6} is preferably linear.

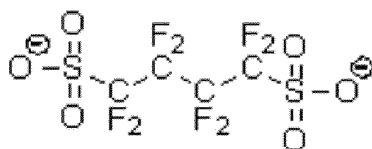
$nb4$ is 1 or 2, preferably 1.

When $nb4$ is 2, R^{b6} becomes divalent, and hydrogen or fluorine becomes a single bond from R^{b6} described above and is bonded to an S atom.

[0044]

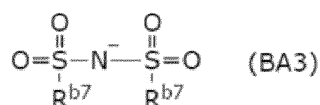
Exemplified embodiments of the formula (BA2) are as follows.

$CF_3SO_3^-$, $C_4F_9SO_3^-$, $C_3F_7SO_3^-$



[0045]

The formula (BA3) is as follows:



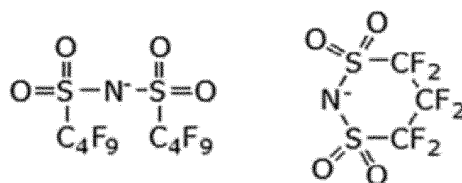
where,

$\text{R}^{\text{b}7}$ is each independently C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl or C_{6-12} fluorine-substituted alkoxyaryl, preferably C_{2-6} fluorine-substituted alkyl. The alkyl moiety of $\text{R}^{\text{b}7}$ is preferably methyl, ethyl, propyl, butyl, or pentyl, more preferably methyl, ethyl, or butyl, further preferably butyl. The alkyl moiety of $\text{R}^{\text{b}7}$ is preferably linear.

Here, two $\text{R}^{\text{b}7}$ can be bonded to each other to form a fluorine-substituted heterocyclic structure. In this case, the heterocycle can be monocyclic or polycyclic, but preferably is a monocyclic structure having 5 to 8 members.

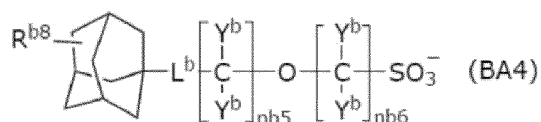
[0046]

Exemplified embodiments of the formula (BA3) are as follows.



[0047]

The formula (BA4) is as follows:



where,

$\text{R}^{\text{b}8}$ 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 carbonyl, oxy, or carbonyloxy, preferably carbonyl or carbonyloxy, more preferably carbonyl.

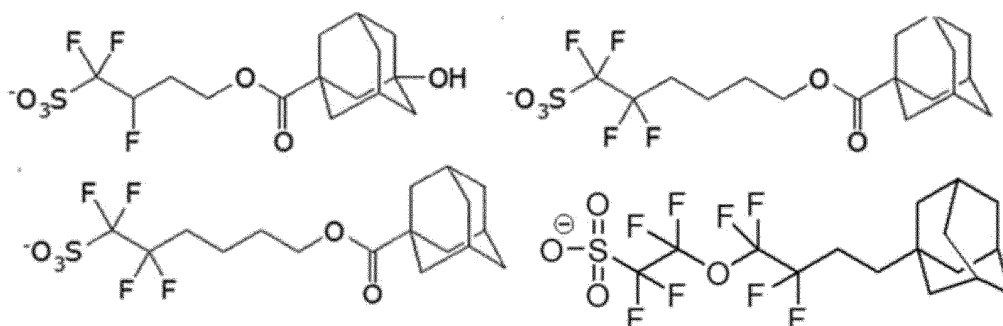
Y^{b} is each independently hydrogen or fluorine, and preferably, at least one or more thereof is fluorine.

$\text{nb}5$ is an integer of 0 to 10, preferably 0.

$\text{nb}6$ is an integer of 0 to 21, preferably 4, 5, or 6.

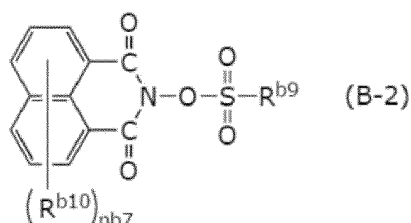
[0048]

Exemplified embodiments of the formula (BA4) are as follows.



[0049]

The formula (B-2) is as follows:



where,

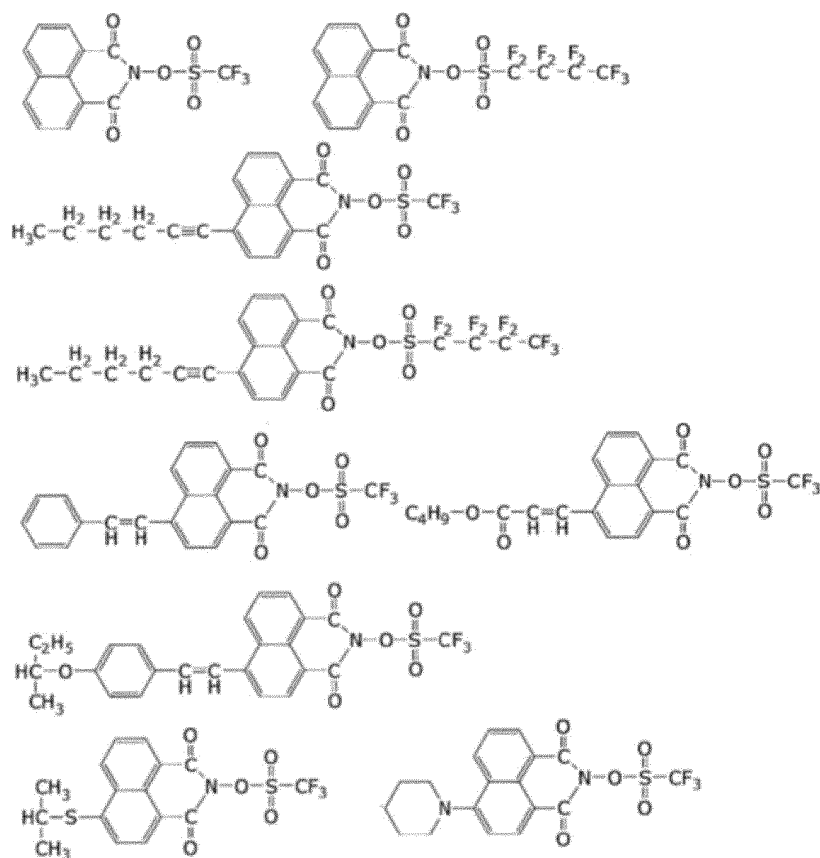
$\text{R}^{\text{b}9}$ is C_{1-5} fluorine-substituted alkyl, preferably, C_{1-4} alkyl in which all hydrogen are substituted with fluorine, more preferably C_1 or C_4 alkyl in which all hydrogen are substituted with fluorine.

$\text{R}^{\text{b}10}$ is each independently C_{3-10} alkenyl or alkynyl (where CH_3- in the alkenyl and alkynyl can be replaced with phenyl, and $-\text{CH}_2-$ in the alkenyl and alkynyl can be replaced with at least one of $-\text{C}(=\text{O})-$, $-\text{O}-$ or phenylene), C_{2-10} thioalkyl, C_{5-10} saturated heterocycle, preferably C_{3-12} alkenyl or alkynyl, or C_{3-5} thioalkyl, C_{5-6} saturated heterocycle; more preferably $-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, $-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{tBu}$, $-\text{CH}=\text{CH}-\text{Ph}$, $-\text{S}-\text{CH}(\text{CH}_3)_2$, $-\text{CH}=\text{CH}-\text{Ph}-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$ and piperidine. Here, tBu means t-butyl and Ph means phenylene or phenyl. In the present invention, alkenyl means a monovalent group having one or more double bonds (preferably one). Similarly, alkynyl means a monovalent group having one or more triple bonds (preferably one).

nb7 is 0, 1 or 2, preferably 0 or 1, and more preferably 0. It is also a preferred embodiment that nb7 = 1 is satisfied.

[0050]

Exemplified embodiments of the formula (B-2) include the followings.



[0051]

The molecular weight of the photoacid generator (B) is preferably 400 to 2,500, more preferably 400 to 1,500.

[0052]

The component (B) may be one or two or more kinds.

The content of the component (B) is preferably more than 0 mass % and 20 mass % or less, 0.05 to 10 mass %, more preferably 0.1 to 5 mass %, further preferably 0.5 to 1.5 mass %, based on the total mass of the component (A).

[0053]

(C) Solvent

The composition according to the present invention comprises a solvent (C).

The solvent (C) contains propylene glycol monomethyl ether (PGME) (C-1), and the content of PGME (C-1) is more than 50 mass % and 100 mass % or less, preferably 60 to 95 mass %, and more preferably 65 to 90 mass %, based on the solvent (C).

[0054]

The solvent (C) preferably further contains a solvent (C-2) other than the solvent (C-1). The solvent (C-2) is selected from the group consisting of an alcohol solvent (C-2-1) and a low boiling point solvent (C-2-2). The alcohol solvent (C-2-1) is a compound in which a hydrogen atom of a chain or alicyclic hydrocarbon is replaced with hydroxy, and in which methylene can be replaced with oxy or carbonyl, and a hydrogen atom can be replaced with aryl.

The content of the solvent (C-2) is 0 mass % or more and less than 50 mass %, preferably 5 to 45 mass %, and more preferably 10 to 35 mass %, based on the solvent (C).

[0055]

The alcohol solvent (C-2-1) is, for example, selected from the group consisting of methanol, ethanol, n-propanol, i-propanol (isopropyl alcohol, IPA), 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, trimethylnonyl alcohol, sec-tetradecyl alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol, methylcyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol, phenylmethylethanol, diacetone alcohol, cresol, ethylene glycol, propylene glycol, 1,3-butyleneglycol, pentanediol-2,4, 2-methylpentanediol-2,4, hexanediol-2,5, heptanediol-2,4, 2-ethyl-1,3-hexanediol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, glycerin, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxytriglycol, 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, 4-methyl-2-pentanol, 3-methyl-2-pentanol, 2-methyl-2-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 4-methyl-2-hexanol, 5-methyl-2-hexanol, 3-methyl-2-hexanol, 2-methyl-2-hexanol, ethyl lactate (EL), propyl lactate, n-butyl lactate, n-amyl lactate, butyric acid, methyl 2-hydroxyisobutyrate, methyl 2-hydroxybutyrate, methyl 3-

hydroxybutyrate, methyl 4-hydroxybutyrate, ethyl 2-hydroxyisobutyrate, ethyl 2-hydroxybutyrate, ethyl 3-hydroxybutyric acid and ethyl 4-hydroxybutyrate; and is preferably IPA and/or EL.

[0056]

The boiling point of the low boiling point solvent (C-2-2) at 1 atm is preferably 80 to 130°C, more preferably 80 to 110°C, and further preferably 80 to 100°C.

The low boiling point solvent (C-2-2) is, for example, selected from the group consisting of n-propanol, i-propanol (IPA), n-butanol, i-butanol, sec-butanol, t-butanol, i-pentanol, 2-methylbutanol, sec-pentanol, t-pentanol, ethylene glycol monomethyl ether, 2-methyl-2-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, propylene glycol dimethyl ether, butyl acetate, methyl ethyl ketone, and methyl isobutyl ketone, and is preferably IPA and/or propylene glycol dimethyl ether.

[0057]

The solvent (C) can further contain a solvent (C-3) other than the solvent (C-1) and the solvent (C-2). Examples of the solvent (C-3) include propylene glycol monomethyl ether acetate (PGMEA) and N-methylpyrrolidone.

The content of the solvent (C-3) is less than 50 mass %, preferably 0 mass % or more and 35 mass % or less, more preferably 0 mass % or more and 10 mass % or less, and further preferably 0 mass % or more and 5 mass % or less, based on the solvent (C). It is also a preferred embodiment of the present invention that the composition contains no solvent (C-3).

[0058]

In the case of forming a resist pattern, it has been found that a scooped-out area tends to be generated at the top of the resist pattern wall when the film thickness increases. According to the present invention, the scooped-out area can be suppressed. This is not bound by theory, but is considered as follows.

When an attempt is made to form a resist film having a very large thickness of 11.0 to 50.0 μm , it is considered that the solvent on the film surface first evaporates and solidifies to play a role like a lid, and a region in which the solvent remains and the density of the solid component (for example, the alkali-soluble resin (A)) of the film decreases may be generated in the lower part of the lid. It is considered that the acid derived from the photoacid generator (B) easily diffuses in the region in which the density decreases, and the acid diffuses even in the unexposed

region from the exposed region.

For example, it is considered that, although being outside the scope of the present invention, in the case of using a resist composition, which contains a large amount of a high boiling point solvent (PGMEA or the like) and uses a low boiling point solvent (PGME or the like) as a sub-solvent, for forming a resist film having a thickness of 11 to 50 μm , when the resist composition is applied to a substrate and then pre-baked, the low boiling point solvent first evaporates to solidify the upper part of the resist film and then plays a role as a lid, so that a part of the high boiling point solvent remains without being evaporated. It is considered that, due to the diffusion of the acid into the region in which the density decreases of such an unexposed region, the portion is largely dissolved at the time of development to have a scooped-out shape.

This is not bound by theory, but is considered as follows. Since a main solvent is PGME, which is a low boiling point solvent, when the composition according to the present invention is used, the phenomenon as described above hardly occurs. When PGME is combined with a solvent selected from the group consisting of low boiling point solvents (C-2-2), it can be avoided that PGME evaporates considerably before the others evaporate, and the solvent is less likely to remain in the resist film. When the alcohol solvent (C-2-1) is combined with PGME, both solvents are alcohol-based, and thus evaporation of the solvent is promoted by an azeotropic phenomenon, so that the solvent hardly remains in the film. When the residual of the solvent in the film is reduced, the diffusion of the acid into the unexposed region is suppressed, the reaction with a developer becomes difficult, and the scooped-out area is suppressed.

[0059]

The content of the solvent (C) is preferably 20 mass % or more and less than 100 mass %, more preferably 50 to 79 mass %, further preferably 55 to 65 mass %, based on the composition.

[0060]

(D) Basic compound

The composition according to the present invention can further contain a basic compound (D). The component (D) can be expected to have an effect of suppressing the diffusion of the acid generated in the exposed region and an effect of suppressing the acid deactivation of the film surface caused by the amine component contained in the air by adding the base to the composition. The component (D) is preferably ammonia, C₁₋₁₆ primary aliphatic amine compounds, C₂₋₃₂ secondary aliphatic amine

compounds, C₃₋₄₈ tertiary aliphatic amine compounds, C₆₋₃₀ aromatic amine compounds, or C₅₋₃₀ heterocyclic amine compounds.

Examples of the C₁₋₁₆ primary aliphatic amine compounds include methylamine, ethylamine, isopropylamine, tert-butylamine, cyclohexylamine, ethylenediamine, and tetraethylenediamine.

Examples of the C₂₋₃₂ secondary aliphatic amine compounds include dimethylamine, diethylamine, methylethylamine, dicyclohexylamine and N,N-dimethylmethylenediamine.

Examples of the C₃₋₄₈ tertiary aliphatic amine compounds include trimethylamine, triethylamine, dimethylethylamine, triisobutylamine, triethanolamine, tri-n-octylamine, tricyclohexylamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'',N''-pentamethyldiethylenetriamine, tris[2-(dimethylamino)ethyl]amine, and tris[2-(2-methoxyethoxy)ethyl]amine.

Examples of the C₆₋₃₀ aromatic amine compounds include aniline, benzylamine, naphthylamine, N-methylaniline, 2-methylaniline, 4-aminobenzoic acid, and phenylalanine.

Examples of the C₅₋₃₀ heterocyclic amine compounds include pyrrole, oxazole, thiazole, imidazole, 4-methylimidazole, pyridine, methylpyridine, butylpyridine, and 1,4-diazabicyclo[2.2.2]octane.

[0061]

The molecular weight of the component (D) is preferably 17 to 500 and more preferably 60 to 400.

The component (D) may be one or two or more kinds.

The content of the component (D) is preferably 0.01 to 3 mass %, more preferably 0.03 to 1 mass %, and further preferably 0.05 to 0.5 mass %, based on the total mass of the component (A).

[0062]

(E) Surfactant

The composition according to the present invention can further contain a surfactant (E). By the component (E), the coatability of the composition can be improved. Examples of the component (E) include nonionic surfactants, anionic surfactants, amphoteric surfactants and the like.

[0063]

Examples of the nonionic surfactant include, polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene oleyl ether and polyoxyethylene cetyl ether, polyoxyethylene fatty acid diesters, polyoxyethylene fatty acid monoesters, polyoxyethylene polyoxypropylene

block polymer, acetylene alcohol, acetylene glycol, polyethoxylate of acetylene alcohol, acetylene glycol derivatives such as polyethoxylate of acetylene glycol, fluorine-containing surfactants, for example, FLUORAD (trade name, 3M Japan), MEGAFACE (trade name: DIC), SURFLON (trade name, AGC), or organosiloxane surfactants, for example, KF-53 (trade name, Shin-Etsu Chemical), and the like. Examples of the acetylene glycol include 3-methyl-1-butyne-3-ol, 3-methyl-1-pentyn-3-ol, 3,6-dimethyl-4-octyne-3,6-diol, 2,4,7,9-tetramethyl- 5-decyne-4,7-diol, 3,5-dimethyl-1-hexyne-3-ol, 2,5-dimethyl-3-hexyne-2,5-diol, 2,5-dimethyl-2,5-hexanediol, and the like.

[0064]

Examples of the anionic surfactant include ammonium salt or organic amine salt of alkyl diphenyl ether disulfonic acid, ammonium salt or organic amine salt of alkyl diphenyl ether sulfonic acid, ammonium salt or organic amine salt of alkyl benzene sulfonic acid, ammonium salt or organic amine salt of polyoxyethylene alkyl ether sulfuric acid, ammonium salt or organic amine salt of alkyl sulfuric acid, and the like.

[0065]

Examples of the amphoteric surfactant include 2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolium betaine, lauric acid amide propyl hydroxysulfone betaine, and the like.

[0066]

The component (E) may be one or two or more kinds.

The content of the component (E) is preferably 0.0001 to 1 mass %, more preferably 0.001 to 1 mass %, and further preferably 0.05 to 0.5 mass %, based on the component (A).

[0067]

(F) Plasticizer

The composition according to the present invention can further contain a plasticizer (F). By containing the component (F), film cracking during thick film formation can be suppressed.

Examples of the component (F) include an alkali-soluble vinyl polymer and an acid-dissociable group-containing vinyl polymer. Exemplified embodiments thereof include polyvinyl chloride, polystyrene, polyhydroxystyrene, polyvinyl acetate, polyvinyl benzoate, polyvinyl ether, polyvinyl butyral, polyvinyl alcohol, polyether ester, polyvinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylic acid ester, polyimide maleate, polyacrylamide, polyacrylonitrile, polyvinyl phenol, novolac, and copolymers thereof, and polyvinyl ether, polyvinyl butyral, and polyether

ester are more preferable.

[0068]

The composition provided by the present invention can obtain favorable physical properties also in the case of having a film thickness of 11 to 50 μm even when the composition contains a small amount of the component (F). The content of the component (F) is preferably 0 to 3 mass %, and more preferably 0 to 1 mass %, based on the composition. It is also a preferred embodiment of the present invention that the composition of the present invention substantially contains no component (F). It is also a preferred embodiment of the present invention that the composition of the present invention contains no component (F) (0.0 mass %). Without wishing to be bound by theory, it is considered that the etching resistance of the resist film, the thermal resistance, and/or the shape of the resist pattern can be improved as the content of the component (F) is small. The improvement of the shape of the resist pattern more preferably means that the shape of the top of the pattern is improved.

[0069]

(G) Additive

The composition according to the present invention can comprise an additive (G) other than (A) to (F). The component (G) is selected from at least one of the group consisting of a surface smoothing agent, a photoreactive quencher, a dye, a contrast enhancer, an acid, a radical generator, a substrate adhesion enhancer and an antifoaming agent.

The content of the component (G) (the sum in the case of a plurality of components (G)) is preferably 0.01 to 10 mass % and more preferably 0.1 to 2 mass %, based on the component (A). It is also a preferred embodiment of the present invention that no component (G) is contained (0 mass %).

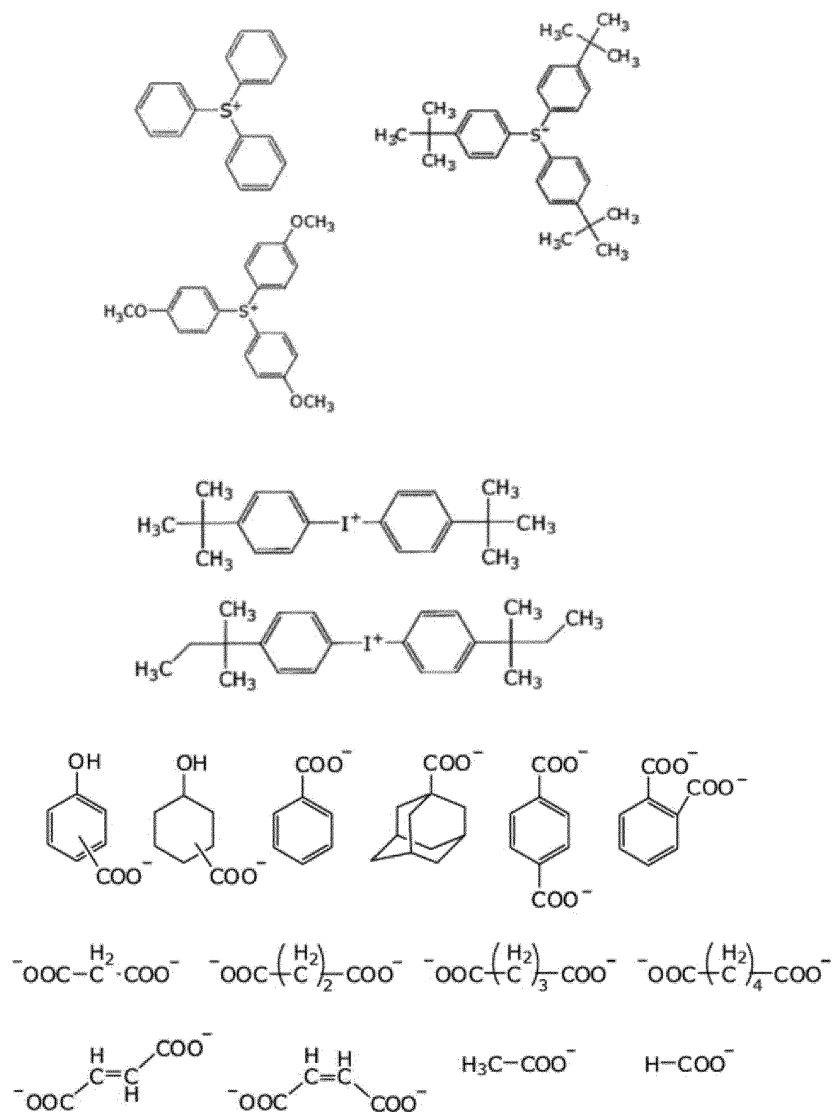
[0070]

The photoreactive quencher can be used to suppress deactivation of the acid of the resist film surface due to a component such as amine contained in the air, and is different from the photoacid generator (B). As a preferred embodiment of the present invention, the acid directly acting on the alkali-soluble resin (A) is not an acid released from the photoreactive quencher but an acid released from the photoacid generator (B).

The photoreactive quencher releases an acid by exposure. The acid preferably has an acid dissociation constant pK_a (H_2O) of 1.5 to 8

(more preferably 1.5 to 5).

The photoreactive quencher is composed of a cation and an anion, and certain cations and anions include the followings.



[0071]

Method for manufacturing a resist film

The method for manufacturing a resist film according to the present invention comprises the following steps:

(1) applying the composition according to the present invention above a substrate; and

(2) heating the composition to form a resist film.

Hereinafter, one embodiment of the manufacturing method

according to the present invention is described.

[0072]

Step (1)

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 the case where a layer is formed directly on a substrate and the case where a layer is formed on a substrate via another layer. For example, a planarization film or resist underlayer can be formed immediately above a substrate, and the composition according to the present invention can be applied immediately above the film. An embodiment in which the composition according to the present invention is applied immediately above a substrate (without intervening other layer) is more preferable. The application method is not particularly limited, and examples thereof include a method using a spinner or a coater.

[0073]

Step (2)

After application of the composition, a resist film is formed by heating (prebaking). The heating in the step (2) 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 here 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 60 to 240 seconds). The heating is preferably performed in an air or a nitrogen gas atmosphere.

The film thickness of the resist film is selected depending on the purpose, but when the composition according to the present invention is used, a pattern having a better shape can be obtained when a coating film having thick film thickness is formed. For this reason, the thickness of the resist film is preferably thicker, for example, preferably 11.0 to 50.0 μm , more preferably 11.0 to 20.0 μm , further preferably 11.0 to 18.0 μm , further more preferably 12.0 to 18.0 μm .

[0074]

A resist pattern can be manufactured by the method further comprising the following steps:

(3) exposing the resist film; and

(4) developing the resist film. Although describing for clarity, the steps (1) and (2) are performed before the step (3). The numbers in

parentheses indicating the step mean the order. The same applies hereinafter.

[0075]

Step (3)

The resist film is exposed through a predetermined mask. The wavelength of light to be used for exposure is not particularly limited, but it is preferable to expose with light having a wavelength of 13.5 to 248 nm. In particular, KrF excimer laser (wavelength: 248 nm), ArF excimer laser (wavelength: 193 nm), extreme ultraviolet ray (wavelength: 13.5 nm), or the like can be used, and KrF excimer laser is preferable. These wavelengths allow a range of $\pm 1\%$. After exposure, post exposure bake (PEB) can also be performed, as necessary. The post exposure baking temperature is preferably 80 to 150°C, more preferably 100 to 140°C, and the heating time is 0.3 to 5 minutes, preferably 0.5 to 2 minutes.

[0076]

Step (4)

The exposed resist film is developed with a developer. As the developing method, a 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 inorganic alkalis, such as sodium hydroxide, potassium hydroxide, sodium carbonate and sodium silicate; organic amines, such as ammonia, ethylamine, propylamine, diethylamine, diethylaminoethanol and triethylamine; quaternary amines, such as tetramethylammonium hydroxide (TMAH); and the like are used, and a 2.38 mass % TMAH aqueous solution is preferable. A surfactant can 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 treatment can also be performed, as necessary. When a positive type resist composition is used, the exposed region is removed by development to form a resist pattern. The resist pattern can also be further made finer, for example, using a shrink material.

[0077]

When a thick film resist pattern is formed using a chemically amplified resist, a scooped-out area may be generated at the top of resist pattern wall, especially when the aspect ratio is high (details of the scooped-out area are explained using Figures in Examples).

In a preferred embodiment, the distance between the perpendicular line drawn from the end point of the top of the resist pattern down to the substrate and the perpendicular line drawn from the most scooped point on the side surface of the resist pattern down to the substrate (hereinafter referred to as the width of bite) is less than 1,200 nm, more preferably 0 nm to less than 800 nm, further preferably 0 nm to less than 500 nm. In the present invention, the scooped-out area can be suppressed. Since the scooped-out area can be suppressed, resistance of the pattern can be strengthened in the subsequent steps, which is advantageous.

[0078]

A processed substrate can be manufactured by a method further comprising the following step:

(5) processing using the resist pattern as a mask.

[0079]

Step (5)

The formed resist pattern is preferably used for processing an underlayer or a substrate (more preferably a substrate). In particular, with the resist pattern as a mask, various substrates that become a base can be processed using a dry etching method, a wet etching method, an ion implantation method, a metal plating method, or the like. It is a more preferable embodiment to etch the substrate by a dry etching method using the resist pattern of the present invention as a mask. Since the resist pattern according to the present invention can increase the film thickness, it can also be used for substrate processing using an ion implantation method.

When processing an underlayer using a resist pattern, the processing can be performed in stages. For example, a BARC layer can be processed using a resist pattern, a SOC film can be processed using the BARC pattern, and a substrate can be processed using the SOC pattern.

[0080]

Thereafter, if necessary, the substrate is further processed, a step of forming a wiring on the processed substrate is preferably conducted, and a device can be manufactured. For these processing, known methods can be applied. If necessary, the substrate is cut into chips, which are connected to a lead frame and packaged with resin. In the present invention, this packaged product is referred to as the device. 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, preferably a semiconductor.

[Example]

[0081]

The present invention is described below with reference to several examples. The embodiment of the present invention is not limited only to these examples.

[0082]

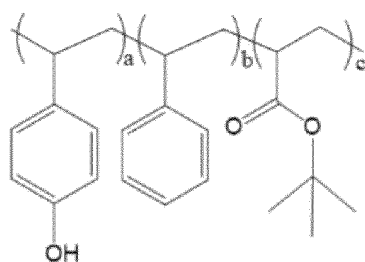
Preparation of Resist Composition 101

PGME and PGMEA are mixed at a mass ratio of 70 : 30 (= PGME : PGMEA) to obtain a mixed solvent. To the mixed solvent (62.0 mass %), the alkali-soluble resin A1 (36.99 mass %), the photoacid generator B1 (0.91 mass %), the basic compound D1 (0.04 mass %), and the surfactant E1 (0.06 mass %) are each added to obtain a mixed solution. The numerical value in parentheses indicates the content of each component with respect to the total mass of the composition. The solid component concentration is 38.0 mass %. These are A1 : B1 : D1 : E1 = 100 : 2.47 : 0.10 : 0.15 in terms of mass ratio.

In the following Examples, components other than the solvent are referred to as solid components, and the concentration of the sum of components other than the solvent in the entire composition is referred to as solid component concentration.

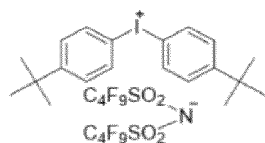
The mixed solution is stirred at room temperature for 30 minutes to obtain a solution. It is visually confirmed that each component is completely dissolved. The obtained solution is filtered through a 0.05 μm filter to obtain Resist Composition 101.

· A1: p-hydroxystyrene/styrene/t-butyl acrylate copolymer (Mw = 27,000, random copolymerization)



$$a : b : c = 60 : 20 : 20$$

· B1: the compound shown below (Sumitomo Pharma Food & Chemical Co., Ltd., ZK-0518)



- D1: tris[2-(2-methoxyethoxy)ethyl]amine
- E1: MEGAFACE R-2011(DIC)

[0083]

Example of resist film

An 8-inch silicon wafer is subjected to an HMDS treatment at 90°C for 60 seconds. Using the coater developer Mark8 (Tokyo Electron), the prepared resist composition is coated by spinning on the 8-inch silicon wafer. The rotation speed of spin coating is changed from 1,000 rpm to 3,500 rpm according to a target film thickness. Baking is performed using a hot plate at 140°C for 180 seconds to obtain a resist film. The film thickness of the obtained resist film is measured using a light-interference film thickness meter (M-1210, SCREEN).

The film thickness of the resist film obtained by performing the above operation and spin-coating Resist Composition 101 (solid component concentration: 38.0 mass %) at 1,000 rpm is 15.0 μm.

In the following Examples, the solid component concentration is adjusted (the mass ratio of each component of the solid component is maintained) or the rotation speed of spin coating is adjusted according to a target film thickness.

In the case of forming a resist film having a film thickness of 8 to 15 μm, Composition 101 having a solid component concentration of 38.0 mass % is used as it is. The rotation speed of spin coating is 1,000 rpm for a film thickness of 15 μm and 3,500 rpm for a film thickness of 8 μm. By gradually increasing the rotation speed, the film thickness to be obtained can be gradually reduced.

In the case of forming a resist film having a film thickness of 4 to 7 μm, the same solvent is added to Composition 101 and Composition 101 in which the solid component concentration is adjusted to 32.0 mass % is used. The rotation speed of spin coating is 1,000 rpm for a film thickness of 7 μm, and a desired film thickness is obtained by gradually increasing the rotation speed.

In the case of forming a resist film having a film thickness of 2 to 3 μm, the same solvent is added to Composition 101 and Composition 101 in which the solid component concentration is adjusted to 19.0 mass % is

used. The rotation speed of spin coating is 1,000 rpm for a film thickness of 3 μm , and a desired film thickness is obtained by gradually increasing the rotation speed.

In the case of forming a resist film having a film thickness of 1 μm , the same solvent is added to Composition 101 and Composition 101 in which the solid component concentration is adjusted to 14.0 mass % is used. The rotation speed of spin coating is 1,000 rpm.

For change in the film thickness, the solid component concentration, and the rotation speed, the same applies to the case of using another composition in which the solid component and the solvent are changed from Composition 101.

[0084]

Example of resist pattern formation

The resist film having a film thickness of 15 μm obtained in the above example of resist film formation is exposed using a KrF stepper (FPA3000-EX5, Canon Inc.). Thereafter, PEB is performed using a hot plate at 110°C for 180 seconds. This film is developed with a 2.38% TMAH aqueous solution (AZ300MIF, Merck Electronics Ltd.) for 60 seconds, and a trench pattern having Line : Space = 3 : 1 and a space width of 5 μm is formed. The cross-sectional shape of the obtained pattern is observed using a scanning electron microscope (S9200, Hitachi) to confirm a pattern shape.

Using Composition 101 (solid component concentration: 38.0 mass %), the operation is performed to form a resist film having a film thickness of 15 μm as in the above example of resist pattern formation, thereby obtaining a resist pattern in which the width of the top of the pattern wall is 7 μm .

In the case of forming a resist pattern from a resist film having another film thickness, exposure is performed under the same conditions as those for the resist film having a film thickness of 15 μm described above.

The pattern shape to be formed will be described with reference to FIGS. 1A and 1B. In FIG. 1A, a resist pattern 12 is formed on a substrate 11, and a line width 13, a space width 14, and a top width 15 are 15 μm , 5 μm , and 7 μm , respectively. A top of pattern wall 16 is an end of the top, and a scooped-out area may be generated at this portion. The resist film thickness of FIG. 1A is 15 μm . FIG. 1B is a schematic view when the film thickness is 5 μm without changing the inclination of the resist pattern. In the evaluation in which the film thickness is changed, a pattern is

manufactured without changing the inclination as described above.

[0085]

Evaluation 1 of the top of the pattern wall

Study to change a solvent is conducted. Using Composition 101 (solid component concentration: 38.0 mass %), a resist film having a film thickness of 15 μm is formed as in the example of resist film formation, and a resist pattern is formed as in the example of resist pattern formation. A slice of the sample is prepared and observed with an SEM.

The degree of being scooped inward from the top of the pattern (the width of bite) is evaluated. In particular, it is explained with reference to FIG. 2. FIG. 2 schematically shows the top of wall 21 of FIGS. 1A and 1B. A line is drawn perpendicularly from the end of the top of the pattern down to the substrate. A line is drawn perpendicularly from the most scooped point on the side surface of the pattern down to the substrate. The distance between each line is taken as the width of bite. The result is designated as Example 101.

The evaluation criteria are shown below.

A: width of bite is less than 500 nm

B: width of bite is 500 nm or more and less than 800 nm

C: width of bite is 800 nm or more and less than 1,200 nm

D: the width of bite, that is, the distance of being scooped is 1,200 nm or more

The evaluation results are shown in Table 1.

Table 1	(C-1)	(C-2)	(C-3)	Mass ratio (C-1):(C-2):(C-3)	Width of bite	
					(nm)	Evaluation
Example 101	PGME	—	PGMEA	70:0:30	966	B
Example 102	PGME	—	—	100:0:0	549	B
Example 103	PGME	IPA	—	85:15:0	559	B
Example 104	PGME	IPA	—	70:30:0	463	A
Example 105	PGME	EL	—	85:15:0	476	A
Example 106	PGME	EL	—	70:30:0	440	A
Example 107	PGME	MMPOM	—	85:15:0	470	A
Example 108	PGME	MMPOM	—	70:30:0	460	A
Comparative Example 101	—	—	PGMEA	0:0:100	1514	D
Comparative Example 102	—	EL	PGMEA	0:30:70	>3000	D

PGME: propylene glycol monomethyl ether (boiling point: 119°C)

PGMEA: propylene glycol 1-monomethyl ether 2-acetate (boiling

point: 146°C)

IPA: isopropyl alcohol (boiling point: 83°C)

EL: ethyl lactate (boiling point: 154°C)

MMPOM: propylene glycol dimethyl ether (boiling point: 97°C)

[0086]

Compositions described in Table 1 are prepared in the same manner as in the preparation example of Resist Composition 101, except that the solvent is changed as shown in Table 1. The solid component and the solid component concentration of 38.0 mass % are not changed. Using these compositions, resist films having a film thickness of 15 μm are formed as described in the example of resist film formation, and resist patterns are formed as described in the example of resist pattern formation. Slices of these samples are prepared and observed with an SEM. Evaluation of Composition 102 corresponds to Example 102. The same applies hereinafter.

The evaluation results are shown in Table 1.

[0087]

Evaluation 2 of the top of the pattern wall

Changing the mixing ratio of the solvent and the resist film thickness is studied. Each solvent obtained by mixing PGME and PGMEA at the ratio described in Table 2 is prepared. In the same manner as in Composition 101, components are added to a solvent to have A1 : B1 : D1 : E1 = 100 : 2.47 : 0.10 : 0.15 in terms of mass ratio, thereby obtaining each composition. The solid component concentration and the rotation speed are changed as described in the example of resist film formation to obtain a resist film having a film thickness of 5 to 15 μm. A resist pattern is formed as in the example of resist pattern formation. Slices of these samples are prepared and observed with an SEM.

The width of bite (nm) is evaluated in the same manner as in the method described in Evaluation 1 of the top of the pattern wall. The results are shown in Table 2.

Table 2

	Film Thickness (μ m)	(C-1)PGME : (C-3) PGMEA					
		100:0		70:30		0:100 (Comparative Example)	
	Reference Example	15	549	B	966	B	1514
	7	132	A	248	A	370	A
Reference Example	5	119	A	232	A	301	A

[0088]

Crack evaluation

Changing the Mw of the polymer and the film thickness is studied. The same resin as the resin A1 is prepared except that the Mw described in Table 3 is prepared. PGME and PGMEA are mixed at a mass ratio of 70 : 30 (= PGME : PGMEA) to obtain a solvent. In the same manner as in Composition 101, components are added to a solvent to have A1 : B1 : D1 : E1 = 100 : 2.47 : 0.10 : 0.15 in terms of mass ratio. The solid component concentration and the rotation speed are changed as described in the example of resist film formation to obtain a target film thickness. Using these resist films, a resist pattern is formed as in the above example of resist pattern formation.

A wafer on which the resist pattern is formed is visually observed. The evaluation criteria are as follows.

A: No crack is found.

B: Cracks are found.

Table 3

Film Thickness	Mw:9000	Mw:12000	Mw:15000	Mw:18622	Mw:23168	Mw:26704
5 μm	A	A	A	A	A	A
6 μm	B	A	A	A	A	A
7 μm	B	A	A	A	A	A
8 μm	B	B	A	A	A	A
9 μm	B	B	A	A	A	A
10 μm	B	B	B	A	A	A
11 μm	B	B	B	A	A	A
12 μm	B	B	B	B	A	A
13 μm	B	B	B	B	A	A
14 μm	B	B	B	B	A	A
15 μm	B	B	B	B	B	A

[0089]

Preparation of Resist Composition 201

The same operation as in the preparation example of Composition 101 is performed except for using 100% of PGME as the solvent to obtain Composition 201 (solid component concentration: 38.0 mass %).

[0090]

Heat resistance

The operation is performed as in the example of resist film formation to form a resist film having a film thickness of 15 μm from Composition 201. The resist film is subjected to an operation as in the example of resist pattern formation to obtain a resist pattern.

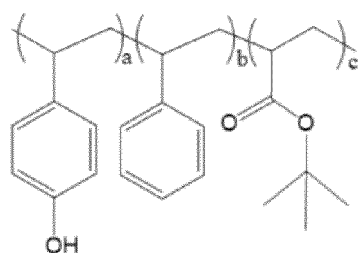
The resist pattern is subjected to additional baking with a changed temperature to prepare a sample. The additional baking time is unified to 60 seconds. Slices of these resist patterns are observed with an SEM. In the case of additional baking at 100°C, no change in resist pattern is confirmed. Similarly, even in the case of additional baking at 120°C and 140°C, no change in resist pattern is confirmed. However, in the case of additional baking at 160°C, a change in the shape of the resist pattern is confirmed. Also in the case of additional baking at 180°C, a change in the shape of the resist pattern is confirmed, and this is considered that the top of the pattern is partially liquefied.

[0091]

Preparation of Resist Composition 301

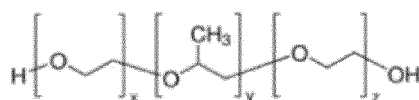
PGME and PGMEA are mixed at a mass ratio of 70 : 30 (= PGME : PGMEA) to obtain a mixed solvent. As the alkali-soluble resin, the following A2 is used. The alkali-soluble resin A2, the photoacid generator B1, the basic compound D1, the surfactant E1, and the plasticizer F1 are added to the solvent at a mass ratio of A1 : B1 : D1 : E1 : F1 = 100 : 2.47 : 0.10 : 0.15 : 20 so that the solid component concentration is 38.0 mass % to obtain a mixed solution. The mixed solution is stirred at room temperature for 30 minutes to obtain a solution. It is visually confirmed that each component is completely dissolved. The obtained solution is filtered through a 0.05 μm filter to obtain Resist Composition 301.

· A2: p-hydroxystyrene/styrene/t-butyl acrylate copolymer (Mw = 18,000, random copolymerization)



$$a : b : c = 60 : 20 : 20$$

· F1



$(x + z) : y = 60 : 40$, block copolymer, Mw: 3,600

[0092]

Etching resistance

The operation is performed as in the example of resist film formation to form a resist film having a film thickness of 15 μm from each of Composition 201 and Composition 301. These resist films are subjected to an operation as in the example of resist pattern formation to obtain a resist pattern.

For etching, an etching apparatus NE-5000N (ULVAC) is used.

In O_2 etching, each film on the wafer is dry-etched at a chamber pressure of 10 Pa, a power of 500 W, a bias of 100 W, and a gas flow rate of O_2 (30 sccm), N_2 (5 sccm), and He (266 sccm) for 30 seconds.

In CF_4 etching, each film on the wafer is dry-etched at a chamber pressure of 10 Pa, a power of 500 W, a bias of 100 W, and a gas flow rate of CF_4 (45 sccm) and He (266 sccm) for 30 seconds.

In the film thickness measurement, the film thickness is measured using a light-interference film thickness meter (M-1210, SCREEN).

The film thickness before etching and the film thickness after etching are measured. A difference between the former and the latter is obtained, and an etching rate per unit time is calculated.

The etching rate of each of O_2 etching and CF_4 etching of Composition 301 is set to 100%. The O_2 etching rate and the CF_4 etching rate of Composition 201 are 75% and 82%, respectively.

When Composition 201 is compared with Composition 301, it can be confirmed that the resist film formed from Composition 201 has higher etching resistance.

[Explanation of symbols]

[0093]

11. substrate

12. resist pattern

13. line width

14. space width

15. top width

16. top of pattern wall

21. top of wall

22. width of bite

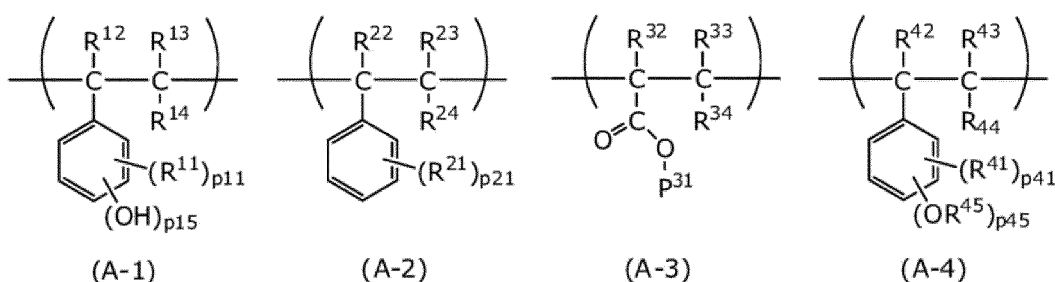
Patent Claims

1. A thick film chemically amplified positive type resist composition comprising an alkali-soluble resin (A), a photoacid generator (B) and a solvent (C):

wherein,

the film thickness of the resist film formed from the thick film chemically amplified positive type resist composition is 11.0 to 50.0 μm ;

the alkali-soluble resin (A) comprises at least one of the following repeating units:



(where,

R^{11} , R^{21} , R^{41} and R^{45} are each independently C_{1-5} alkyl (in which $-CH_2-$ in the alkyl can be replaced with $-O-$);

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 (in which all or part of the alkyl can form a ring, and all or part of H in the alkyl can be substituted with halogen)); and

the solvent (C) comprises propylene glycol monomethyl ether (PGME) (C-1), and the content of PGME (C-1) is more than 50 mass % and 100 mass % or less, based on the solvent (C).

2. The composition according to claim 1, wherein the solvent (C) further comprises a solvent (C-2):

wherein,

the solvent (C-2) is selected from the group consisting of alcohol solvents (C-2-1) and low boiling point solvents (C-2-2).

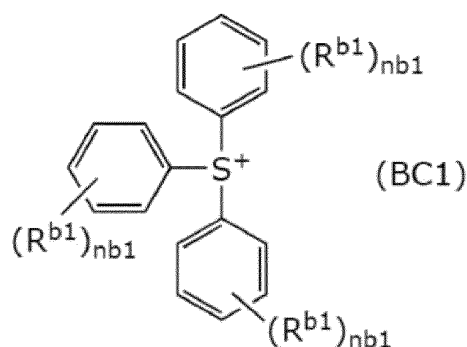
3. The composition according to claim 1 or 2, wherein the alkali-soluble resin (A) has a mass average molecular weight of 12,000 to 50,000.
4. The composition according to one or more of claims 1 to 3, wherein n_{A-1} , n_{A-2} , n_{A-3} and n_{A-4} , which are the numbers of repeating units of the repeating units (A-1), (A-2), (A-3) and (A-4) in the alkali-soluble resin (A), satisfy the following:
- $$n_{A-1} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 40 \text{ to } 80\%,$$
- $$n_{A-2} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0 \text{ to } 40\%,$$
- $$n_{A-3} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0 \text{ to } 40\%, \text{ or}$$
- $$n_{A-4} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0 \text{ to } 40\%:$$
- optionally, n_{total} , which is the total number of all repeating units contained in the alkali-soluble resin (A), satisfies the following:
- $$(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) / n_{\text{total}} = 80 \text{ to } 100\%.$$
5. The composition according to one or more of claims 1 to 4, wherein the photoacid generator (B) is represented by the formula (B-1) or formula (B-2):



where,

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 $B^{n+}\text{cation}$ as a whole is n-valent, and n is 1 to 3, and

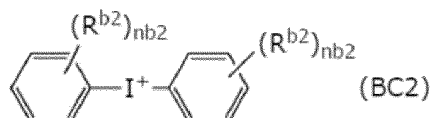
the $B^{n-}\text{anion}$ is an anion represented by the formula (BA1), an anion represented by the formula (BA2), an anion represented by the formula (BA3), or an anion represented by the formula (BA4), and the $B^{n-}\text{anion}$ as a whole is n-valent:



(where,

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

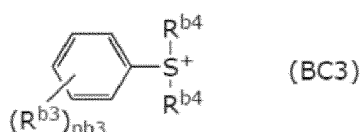
$nb1$ is each independently 0, 1, 2 or 3);



(where,

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);

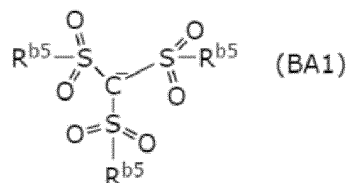


(where,

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

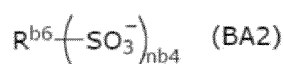
R^{b4} is each independently C_{1-6} alkyl; and

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



(where,

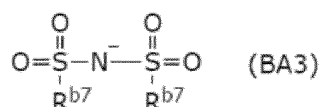
R^{b5} is each independently C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, or C_{1-6} alkyl);



(where,

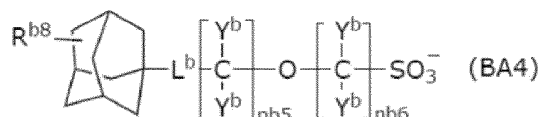
R^{b6} is C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl or C_{6-12} fluorine-substituted alkoxyaryl; and

$nb4$ is 1 or 2);



(where,

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



(where,

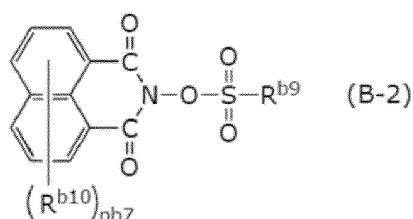
R^{b8} is hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy or hydroxy,

L^b is carbonyl, oxy or carbonyloxy;

Y^b is each independently hydrogen or fluorine;

$nb5$ is an integer of 0 to 10; and

$nb6$ is an integer of 0 to 21); and



where,

R^{b9} is C_{1-5} fluorine-substituted alkyl;

R^{b10} is each independently C_{3-10} alkenyl or alkynyl (in which CH_3 - in the alkenyl and alkynyl can be substituted with phenyl, and $-CH_2-$ in the alkenyl and alkynyl can be replaced with at least one of $-C(=O)-$, $-O-$ or phenylene), C_{2-10} thioalkyl, C_{5-10} saturated heterocycle; and

$nb7$ is 0, 1 or 2.

6. The composition according to one or more of claims 1 to 5, further comprising a basic compound (D):

optionally, the base compound (D) is ammonia, C_{1-16} primary aliphatic amine compounds, C_{2-32} secondary aliphatic amine compounds, C_{3-48} tertiary aliphatic amine compounds, C_{6-30} aromatic amine compounds, or C_{5-30} heterocyclic amine compounds.

7. The composition according to one or more of claims 1 to 6, further comprising a surfactant (E):

optionally, a plasticizer (F) is further comprised; or

optionally, an additive (G) is further comprised, and the additive (G) is at least one selected from the group consisting of a surface smoothing agent, a photoreactive quencher, a dye, a contrast enhancer, an acid, a radical generator, a substrate adhesion enhancer and an antifoaming agent.

8. The composition according to one or more of claims 1 to 7, wherein,

the content of the alkali-soluble resin (A) is more than 0 mass % and 50 mass % or less, based on the composition;

the content of the photoacid generator (B) is more than 0 mass % and 20 mass % or less, based on the alkali-soluble resin (A); and

the content of the solvent (C) is 20 mass % or more and less than 100 mass %, based on the composition:

optionally, the content of the basic compound (D) is 0.01 to 3 mass % based on the alkali-soluble resin (A);

optionally, the content of the surfactant (E) is 0.0001 to 1 mass % based on the alkali-soluble resin (A);

optionally, the content of the plasticizer (F) is 0 to 3 mass % based on the composition; or

optionally, the content of the additive (G) is 0.01 to 10 mass % based on the alkali-soluble resin (A).

9. The composition according to one or more of claims 1 to 8, wherein,

the alcohol solvent (C-2-1) is selected from the group consisting of 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, trimethylnonyl alcohol, sec-tetradecyl alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol, methylcyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol, phenylmethylethanol, 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-ethyl-1,3-hexanediol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, glycerin, ethylene glycol monomethyl ether, ethylene

glycol monoethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxytriglycol, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono propyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, 4-methyl-2-pentanol, 3-methyl-2-pentanol, 2-methyl-2-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 4-methyl-2-hexanol, 5-methyl-2-hexanol, 3-methyl-2-hexanol, 2-methyl-2-hexanol, ethyl lactate, propyl lactate, n-butyl lactate, n-amyl lactate, butyric acid, methyl 2-hydroxyisobutyrate, methyl 2-hydroxybutyrate, methyl 3-hydroxybutyrate, methyl 4-hydroxybutyrate, ethyl 2-hydroxyisobutyrate, ethyl 2-hydroxybutyrate, ethyl 3-hydroxybutyric acid and ethyl 4-hydroxybutyrate; and

the low boiling point solvent (C-2-2) has a boiling point of 80 to 130°C under 1 atmosphere:

optionally, the low boiling point solvent (C-2-2) is selected from the group consisting n-propanol, i-propanol, n-butanol, i-butanol, sec-butanol, t-butanol, i-pentanol, 2-methylbutanol, sec-pentanol, t-pentanol, ethylene glycol monomethyl ether, 2-methyl-2-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, propylene glycol dimethyl ether, butyl acetate, methyl ethyl ketone and methyl isobutyl ketone.

10. The composition according to one or more of claims 1 to 9, which is a thick film chemically amplified positive type KrF resist composition.

11. A method for manufacturing a resist film comprising the following steps:

(1) applying the composition according to one or more of claims 1 to 10 above a substrate; and

(2) heating the composition to form a resist film:

optionally, the film thickness of the resist film is 11.0 μm to 20 μm ;

optionally, the heating in (2) is performed at 100 to 250°C and/or for 30 to 300 seconds; or

optionally, the heating in (2) is performed in the air or in a nitrogen gas atmosphere.

12. A method for manufacturing a resist pattern comprising the following steps:
forming a resist film by the method according to claim 11;
(3) exposing the resist film; and
(4) developing the resist film.
13. The method for manufacturing a resist pattern according to claim 12, wherein the distance between a perpendicular line from the end point of the top of the resist pattern to the substrate and a perpendicular line from the most recessed point of the side surface of the resist pattern to the substrate is less than 1,200 nm.
14. A method for manufacturing a processed substrate comprising the following steps:
forming a resist pattern by the method according to claim 12 or 13; and
(5) processing by using the resist pattern as a mask:
optionally, processing the underlayer or substrate in (5).
15. A method for manufacturing a device comprising the method according to one or more of claims 11 to 14:
optionally, a step of forming a wiring on the processed substrate is further comprised; or
optionally, the device is a semiconductor device.