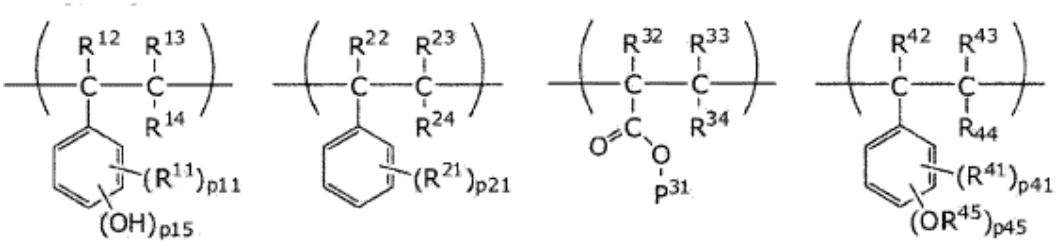
Patent Claims

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

wherein

cLogP of the alkali-soluble resin (A) is 2.76 to 3.35, and the alkali-soluble resin (A) comprises at least one of the following repeating units:



(A-1) (A-2) (A-3) (A-4)

where

R^{11}, R^{21}, R^{41} and R^{45} are each independently C_{1-5} alkyl where $-CH_2-$ 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 H, C_{1-5} alkyl, C_{1-5} 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 C_{4-20} alkyl where a part or all of the alkyl can form a ring, and a part or all of H in the alkyl can be replaced with halogen,

wherein the number of the repeating units n_{A-1}, n_{A-2}, n_{A-3} and n_{A-4} of the repeating units (A-1), (A-2), (A-3) and (A-4) in the alkali-soluble resin (A) satisfies the following:

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

$n_{A-2} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ = 5 to 35%,

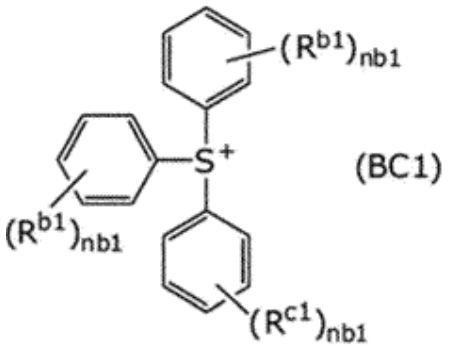
$n_{A-3} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ = 0 to 40%, or $n_{A-4} / (n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ = 0 to 40%.

2. The chemically amplified resist composition according to claim 1, wherein the photoacid generator (B) is represented by the formula (B-1) or the formula (B-2):

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

wherein

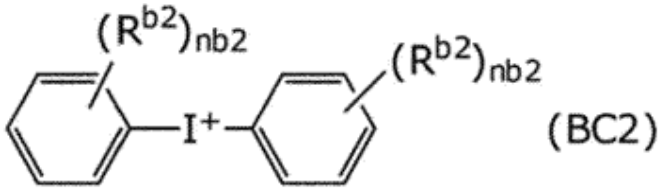
the B^{n+}cation is a cation represented by the formula (BC1), a cation represented by the formula (BC2) or a cation represented by the formula (BC3), the B^{n+}cation is n valent as a whole, and n is 1 to 3, and the B^{n-}anion is an anion represented by the formula (BA1), an anion represented by the 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:



where

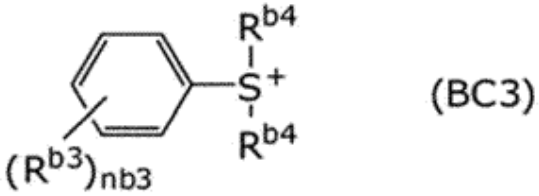
R^{b1} is each independently C_{1-6} alkyl, C_{1-6} alkoxy, C_{6-12} aryl, C_{6-12} arylthio or C_{6-12} aryloxy, and

nbl is each independently 0, 1, 2 or 3;



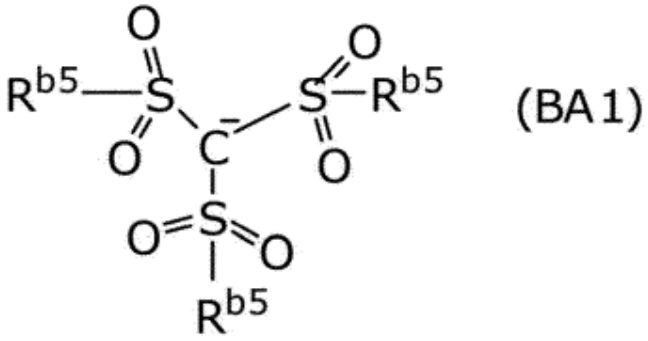
where

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;



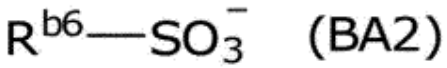
where

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

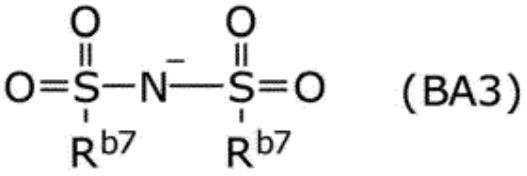
R^{b5} is each independently fluorine-substituted C_{1-6} alkyl, fluorine-substituted C_{1-6} alkoxy, or C_{1-6} alkyl;



(BA2)

where

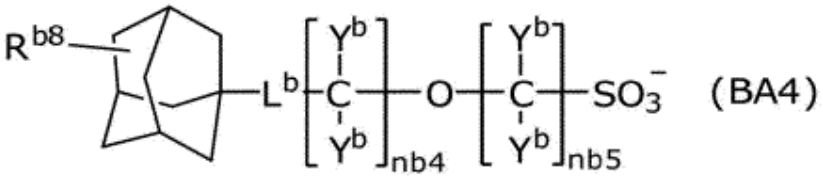
R^{b6} is fluorine-substituted C_{1-6} alkyl, fluorine-substituted C_{1-6} alkoxy, fluorine-substituted C_{6-12} aryl, fluorine-substituted C_{2-12} acyl or fluorine-substituted C_{6-12} alkoxyaryl;



(BA3)

where

R^{b7} is each independently fluorine-substituted C1-6 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, where two R^{b7} can be bonded to each other to form a fluorine-substituted heterocyclic structure;



(BA4)

where

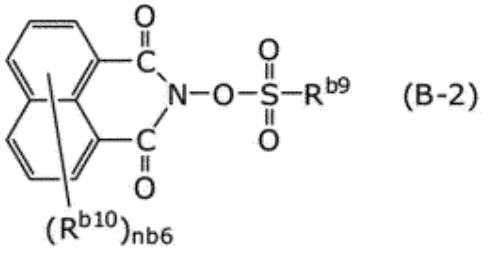
R^{b8} is hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy or hydroxy,

L^b is carbonyl, oxy or carbonyloxy,

Y^b is each independently hydrogen or fluorine,

nb4 is an integer of 0 to 10, and

nb5 is an integer of 0 to 21;



(B-2)

where

R^{b9} is fluorine-substituted C_{1-5} alkyl, R^{b10} is each independently C_{3-10} alkenyl or alkynyl (where CH_3- in the alkenyl and alkynyl can be replaced with phenyl, and -CH_2- in the alkenyl and alkynyl can be replaced with at least one of -C(=O)-, -0- or phenylene), C_{2-10} thioalkyl, C_{5-10} saturated heterocycle, and

nb6 is 0, 1 or 2.

3. The chemically amplified resist composition according to claim 1 or 2, further comprising a photoacid generator (D), wherein the photoacid generator (D) is represented by the formula (D-1):

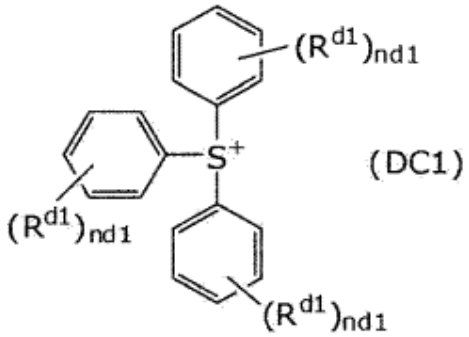
D^{m+}cation D^{m-}anion (D-1)

where

the D^{m+}cation is a cation represented by the formula (DC1) or a cation represented by the formula (DC2), and the D^{m+}cation is m valent as a whole,

m is 1 to 3, and

the D^{m-}anion is an anion represented by the formula (DA1) or an anion represented by the formula (DA2), and the D^{m-}anion is m valent as a whole:

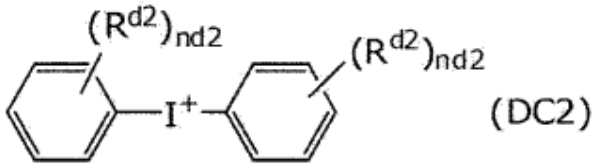


(DC1)

where,

R^{d1} is each independently C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl, and

nd1 is each independently 0, 1, 2 or 3;

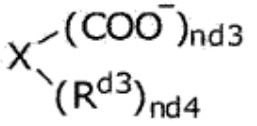


(DC2)

where

R^{d2} is each independently C_{1-6} alkyl, C_{1-6} alkoxy or C_{6-12} aryl, and

nd2 is each independently 0, 1, 2 or 3;



(DA1)

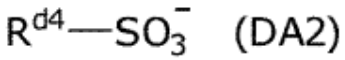
where

X is C_{1-20} hydrocarbon or a single bond,

R^{d3} is each independently hydrogen, hydroxy, C_{1-6} alkyl, or C_{6-10} aryl,

nd3 is 1, 2 or 3, and

nd4 is 0, 1 or 2;



(DA2)

where

R^{d4} is C_{1-15} alkyl (where a part or all of the alkyl can form a ring and $-CH_2-$ in the alkyl can be replaced with -C(=O)-) :

preferably, the cation moiety generated by the photoacid generator (D)when receives light is a quencher that reacts with the anion moiety generated by the photoacid generator (B) when receives light.

4. The chemically amplified resist composition according to claim 1 or 2, further comprising a basic compound (E):

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

5. The chemically amplified resist composition according to claim 1 or 2, further comprising a surfactant (F):

preferably, the chemically amplified resist composition further comprises an additive (G),

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

6. The chemically amplified resist composition according to claim 1 or 2, assuming that the total number of all repeating units contained in the alkali-soluble resin (A) is n_{total}, following is satisfied:

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

7. The chemically amplified resist composition according to claim 1 or 2, wherein the photoacid generator (B) releases an acid having an acid dissociation constant pKa (H_2O) of -20 to 1.4 upon exposure:

preferably, the photoacid generator (D) releases a weak acid having an acid dissociation constant pKa (H_2O) of 1.5 to 8 upon exposure, or

preferably, the base dissociation constant pKb (H_2O) of the basic compound (E) is -12 to 5.

8. The chemically amplified resist composition according to claim 1 or 2, wherein the content of the alkali-soluble resin (A) is more than 0 mass % and 20 mass % or less, based on the chemically amplified resist 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 80 mass % or more and less than 100 mass %, based on the chemically amplified resist composition:

preferably, the content of the photoacid generator (D) is 0.01 to 5 mass %, based on the alkali-soluble resin (A), preferably, the content of the basic compound (E) is 0.01 to 3 mass %, based on the alkali-soluble resin (A), preferably, the content of the surfactant (F) is more than 0 mass % and 1 mass % or less, based on the alkali-soluble resin (A), or

preferably, the alkali-soluble resin (A) has a mass average molecular weight of 1,000 to 50,000.

9. The chemically amplified resist composition according to claim 1 or 2, wherein the solvent (C) is water, a hydrocarbon solvent, an ether solvent, an ester solvent, an alcohol solvent, a ketone solvent, or a combination of any of these.

10. The chemically amplified resist composition according to claim 1 or 2, which is a thin film chemically amplified resist composition:

preferably, the thin film chemically amplified resist composition is a thin film KrF chemically amplified resist composition:

preferably, the thin film chemically amplified resist composition is a thin film positive type chemically amplified resist composition; or

preferably, the thin film chemically amplified resist composition is a thin film KrF positive type chemically amplified resist composition.

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

(1) applying the composition according to claim 1 or 2 above a substrate; and

(2) heating the composition to form a resist film: preferably, the film thickness of the resist film is 50 nm to 1,000 nm;

preferably, the heating in the step (2) is performed at 100 to 250°C and/or for 30 to 300 seconds; or preferably, the heating in the step (2) is performed in an atmosphere or 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 assuming that the height from the top to the bottom of the resist pattern is T, the resist width at the height from the bottom of the resist pattern of 0.5T is $W_{0.5}$, the height at which resist width is $0.99W_{0.5}$ is T', and the difference between the height T and the height T' is Tr,

Tr/T = 0 to 25% is satisfied.

14. A method for manufacturing a processed substrate comprising the following steps:

forming a resist pattern by the method according to claim 12; and

(5) processing using the resist pattern as a mask: preferably, in the step (5), the underlayer film or the substrate is processed.

15. A method for manufacturing a device comprising the method according to claim 11: preferably, a step of forming a wiring on the processed substrate is further comprised; or

preferably, the device is a semiconductor device.