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### ONIUM SALT, CHEMICALLY AMPLIFIED RESIST COMPOSITION AND PATTERN FORMING PROCESS

#### Abstract

An onium salt consisting of an aromatic carboxylic acid anion including a partial structure having iodine and a cyclic ether structure and an onium cation is provided. When processed by photolithography using high-energy radiation, a chemically amplified resist composition comprising the onium salt has advantages including high sensitivity, high resolution, improved lithography properties, and collapse resistance.

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## Background/Summary

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This non-provisional application claims priority under 35 U.S.C. § 119(a) on Patent Application No. 2024-022661 filed in Japan on Feb. 19, 2024, the entire contents of which are hereby incorporated by reference.

### TECHNICAL FIELD

[0002] This invention relates to an onium salt, a chemically amplified resist composition, and a patterning process.

### BACKGROUND ART

[0003] To meet the demand for higher integration density and operating speed of LSIs, the effort to reduce the pattern rule is in rapid progress. As the use of 5G high-speed communications and artificial intelligence (AI) is widely spreading, high-performance devices are needed for their processing. As the advanced miniaturization technology, manufacturing of microelectronic devices at the 5-nm node by the lithography using EUV of wavelength 13.5 nm has been implemented in a mass scale. Studies are made on the application of EUV lithography to 3-nm node devices of the next generation and 2-nm node devices of the next-but-one generation.

[0004] As the feature size reduces, image blurs due to acid diffusion become a problem. To insure resolution for fine patterns with a size of 45 nm et seq., not only an improvement in dissolution contrast is important as previously reported, but the control of acid diffusion is also important as reported in Non-Patent Document 1. Since chemically amplified resist compositions are designed such that sensitivity and contrast are enhanced by acid diffusion, an attempt to minimize acid diffusion by reducing the temperature and/or time of post-exposure bake (PEB) fails, resulting in drastic reductions of sensitivity and contrast.

[0005] A triangular tradeoff relationship among sensitivity, resolution, and edge roughness (LWR) has been pointed out. Specifically, a resolution improvement requires to suppress acid diffusion whereas a short acid diffusion distance leads to a decline of sensitivity.

[0006] The addition of an acid generator capable of generating a bulky acid is an effective means for suppressing acid diffusion. It was then proposed to incorporate repeat units derived from an onium salt having a polymerizable unsaturated bond in a polymer. Since this polymer functions as an acid generator, it is referred to as polymer-bound acid generator. Patent Document 1 discloses a sulfonium or iodonium salt having a polymerizable unsaturated bond, capable of generating a specific sulfonic acid. Patent Document 2 discloses a sulfonium salt having a sulfonic acid directly attached to the backbone.

[0007] Resist compositions adapted for the ArF lithography are typically based on (meth)acrylate polymers having acid labile groups. These acid labile groups undergo deprotection reaction when an acid generator capable of generating a sulfonic acid which is substituted at  $\alpha$ -position with fluorine (referred to as “ $\alpha$ -fluorinated sulfonic acid,” hereinafter) is used, but not when an acid generator capable of generating a sulfonic acid which is not substituted at  $\alpha$ -position with fluorine (referred to as “ $\alpha$ -non-fluorinated sulfonic acid,” hereinafter) or carboxylic acid is used. When a sulfonium or iodonium salt capable of generating  $\alpha$ -fluorinated sulfonic acid is mixed with a sulfonium or iodonium salt capable of generating  $\alpha$ -non-fluorinated sulfonic acid, the sulfonium or iodonium salt capable of generating  $\alpha$ -non-fluorinated sulfonic acid undergoes ion exchange with the  $\alpha$ -fluorinated sulfonic acid. Through the ion exchange, the  $\alpha$ -fluorinated sulfonic acid once generated upon light exposure is converted back to the sulfonium or iodonium salt. Then the sulfonium or iodonium salt of  $\alpha$ -non-fluorinated sulfonic acid or carboxylic acid functions as a quencher. Patent Document 3 discloses a resist composition comprising a sulfonium or iodonium salt capable of generating carboxylic acid as the quencher.

[0008] Sulfonium salt type quenchers capable of generating carboxylic acid are known. Proposed thus far are sulfonium salts of salicylic acid and  $\beta$ -hydroxycarboxylic acid (Patent Document 4), salicylic acid derivatives (Patent Documents 5 and 6), fluorosalicylic acids (Patent Document 7), hydroxynaphthoic acid (Patent Document 8), salicylic acids having an iodized aromatic substituent group introduced therein (Patent Document 9), and salicylic acids having a cyclic acetal structure introduced therein (Patent Document 10). Salicylic acid is quite effective for suppressing acid diffusion due to the intramolecular hydrogen bond of carboxy group and hydroxy group.

[0009] It is pointed out that the agglomeration of a quencher causes to degrade the dimensional uniformity or CDU of resist patterns. It is thus expected that the CDU of resist patterns after development is improved by preventing the quencher from agglomerating in the resist film, for achieving a uniform distribution of the quencher.

[0010] In connection with the demand for further miniaturization, there is a problem that upon development of a positive resist film in an alkaline developer, the resist film is swollen with the developer so that pattern collapse may occur upon small-size pattern formation. To solve the problem associated with miniaturization, the development of an effective material for a new resist composition is important. It is desired to have an onium salt type quencher having a high sensitivity, fully controlled acid diffusion, acceptable solvent solubility, and effective prevention of pattern collapse.

#### CITATION LIST

[0011] Patent Document 1: JP-A 2006-045311 (U.S. Pat. No. 7,482,108) [0012] Patent Document 2: JP-A 2006-178317 [0013] Patent Document 3: JP-A 2007-114431 [0014] Patent Document 4: WO 2018/159560 [0015] Patent Document 5: JP-A 2020-203984 [0016] Patent Document 6: JP-A 2020-091404 [0017] Patent Document 7: JP-A 2020-091312 [0018] Patent Document 8: JP-A 2019-120760 [0019] Patent Document 9: JP-A 2022-077505 [0020] Patent Document 10: WO 2023/189502 [0021] Non-Patent Document 1: SPIE Vol. 6520 65203L-1 (2007)

#### SUMMARY OF THE INVENTION

[0022] In conjunction with the demand for higher resolution of resist patterns, a prior art resist composition comprising an acid generator of sulfonium salt type and a quencher fails to fully suppress acid diffusion. This raises the problem that lithography properties including contrast, exposure latitude (EL), LWR, CDU, and DOF are degraded. Another problem arising upon formation of small-size patterns is pattern collapse by swell.

[0023] An object of the invention is to provide a novel onium salt and a chemically amplified resist composition comprising the onium salt, the resist composition exhibiting a high sensitivity, high resolution, improved lithography properties including EL, LWR, CDU and DOF, and collapse resistance, when processed by lithography using high-energy radiation such as deep UV, EB, or EUV, independent of whether it is of positive or negative tone. Another object is to provide a pattern forming process using the resist composition.

[0024] The inventor has found that an onium salt containing an aromatic carboxylic acid anion including a partial structure having iodine and a cyclic ether structure has solvent solubility, and that a chemically amplified resist composition comprising the onium salt as a quencher exhibits a high sensitivity, high contrast, improved lithography properties including EL, LWR, CDU and DOF, and collapse resistance upon formation of small-size patterns.

[0025] In one aspect, the invention provides an onium salt consisting of an aromatic carboxylic acid anion including a partial structure having iodine and a cyclic ether structure and an onium cation.

[0026] The preferred onium salt has the formula (1).

##STR00001##

[0027] Herein  $n_1$  is 0 or 1,  $n_2$  is an integer of 1 to 4,  $n_3$  is an integer of 1 to 4,  $n_4$  is an integer of 0 to 3,  $n_2+n_3+n_4$  is from 2 to 5 when  $n_1=0$ ,  $n_2+n_3+n_4$  is from 2 to 7 when  $n_1=1$ ,

[0028] W<sub>sup</sub>.A is a C<sub>sub</sub>.2-C<sub>sub</sub>.10 group containing a cyclic ether structure,

[0029] R.sup.1 is halogen exclusive of iodine, or a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, and when n<sub>4</sub> is 2 or 3, a plurality of R.sup.1 may bond together to form a ring with the carbon atoms on the aromatic ring to which they are attached, some —CH.sub.2— in the ring may be replaced by —O— or —S—,

[0030] L.sup.A and L.sup.B are each independently a single bond, ether bond, thioether bond, ester bond, amide bond, sulfonate ester bond, carbonate bond or carbamate bond,

[0031] X.sup.L is a single bond or a C.sub.1-C.sub.40 hydrocarbylene group which may contain a heteroatom, and

[0032] Z.sup.+ is an onium cation.

[0033] Preferably, L.sup.A is an ether bond or thioether bond.

[0034] Also preferably, W.sup.A is an optionally substituted oxirane ring, optionally substituted oxetane ring, optionally substituted tetrahydrofuran ring or optionally substituted tetrahydropyran ring.

[0035] In a preferred embodiment, Z.sup.+ is a sulfonium cation having the formula (cation-1), iodonium cation having the formula (cation-2) or ammonium cation having the formula (cation-3).

##STR00002##

[0036] Herein R.sup.ct1 to R.sup.ct9 are each independently halogen or a C.sub.1-C.sub.30 hydrocarbyl group which may contain a heteroatom, any two of R.sup.ct1 to R.sup.ct3 may bond together to form a ring with the sulfur atom to which they are attached, and any two of R.sup.ct6 to R.sup.ct9 may bond together to form a ring with the nitrogen atom to which they are attached.

[0037] A quencher in the form of the onium salt defined herein is also provided.

[0038] In a further aspect, the invention provides a chemically amplified resist composition comprising the quencher defined above.

[0039] In a preferred embodiment, the resist composition further comprises a base polymer comprising repeat units having the formula (a1).

##STR00003##

[0040] Herein R.sup.A is hydrogen, fluorine, methyl or trifluoromethyl,

[0041] X.sup.1 is a single bond, phenylene group, naphthylene group or \*—C(=O)—O—X.sup.11 —, the phenylene or naphthylene group may be substituted with an optionally fluorinated C.sub.1-C.sub.10 alkoxy moiety or halogen, X.sup.11 is a C.sub.1-C.sub.10 saturated hydrocarbylene group which may contain a hydroxy moiety, ether bond, ester bond or lactone ring, or phenylene or naphthylene group, \* designates a point of attachment to the carbon atom in the backbone, and

[0042] AL.sup.1 is an acid labile group.

[0043] The base polymer may further comprise repeat units having the formula (a2).

##STR00004##

[0044] Herein R.sup.A is hydrogen, fluorine, methyl or trifluoromethyl, [0045] X.sup.2 is a single bond or \*—C(=O)—O—, \* designates a point of attachment to the carbon atom in the backbone,

[0046] R.sup.11 is halogen, cyano, a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, a C.sub.1-C.sub.20 hydrocarbyloxy group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyl group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyloxy group which may contain a heteroatom, or a C.sub.2-C.sub.20 hydrocarbyloxycarbonyl group which may contain a heteroatom, [0047] AL.sup.2 is an acid labile group, and [0048] a is an integer of 0 to 4.

[0049] The base polymer may further comprise repeat units having the formula (b1) or (b2).

##STR00005##

[0050] Herein R.sup.A is each independently hydrogen, fluorine, methyl or trifluoromethyl, [0051] Y.sup.1 is a single bond or \*—C(=O)—O—, \* designates a point of attachment to the carbon atom in the backbone, [0052] R.sup.21 is hydrogen or a C.sub.1-C.sub.20 group containing at least one structure selected from the group consisting of hydroxy other than phenolic hydroxy, cyano, carbonyl, carboxy, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring,

sultone ring and carboxylic anhydride ( $\text{—C(=O)—O—C(=O)—}$ ), [0053] R.sup.22 is halogen, hydroxy, nitro, cyano, a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, a C.sub.1-C.sub.20 hydrocarbyloxy group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyl group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyloxy group which may contain a heteroatom, or a C.sub.2-C.sub.20 hydrocarbyloxycarbonyl group which may contain a heteroatom, [0054] b is an integer of 1 to 4, c is an integer of 0 to 4, and b+c is from 1 to 5.

[0055] The base polymer may further comprise repeat units of at least one type selected from repeat units having the formulae (c1) to (c4).

##STR00006##

[0056] Herein R.sup.A is each independently hydrogen, fluorine, methyl or trifluoromethyl, [0057] Z.sup.1 is a single bond or optionally substituted phenylene group, [0058] Z.sup.2 is a single bond,  $\text{**—C(=O)—O—Z.sup.21—}$ ,  $\text{**—C(=O)—NH—Z.sup.21—}$ , or  $\text{**-Q—Z.sup.21—}$ , Z.sup.21 is a C.sub.1-C.sub.6 aliphatic hydrocarbylene group, phenylene group or a divalent group obtained by combining the foregoing, which may contain halogen, a carbonyl moiety, ester bond, ether bond or hydroxy moiety, [0059] Z.sup.3 is a single bond, ether bond, ester bond, amide bond, sulfonate ester bond, sulfonamide bond, carbonate bond or carbamate bond, [0060] Z.sup.4 is a single bond, or a C.sub.1-C.sub.6 aliphatic hydrocarbylene group, phenylene group or a divalent group obtained by combining the foregoing, which may contain halogen, carbonyl moiety, ester bond, ether bond or hydroxy moiety, [0061] Z.sup.5 is each independently a single bond, optionally substituted phenylene group, naphthylene group, or  $\text{*—C(=O)—O—Z.sup.51—}$ , Z.sup.51 is a C.sub.1-C.sub.10 aliphatic hydrocarbylene group which may contain halogen, hydroxy moiety, ether bond, ester bond or lactone ring, or phenylene or naphthylene group, [0062] Z.sup.6 is a single bond, ether bond, ester bond, amide bond, sulfonate ester bond, sulfonamide bond, carbonate bond or carbamate bond, [0063] Z.sup.7 is each independently a single bond,  $\text{***—Z.sup.71—C(=O)—O—}$ ,  $\text{***—C(=O)—NH—Z.sup.71—}$ , or  $\text{***—O—Z.sup.71—}$ , Z.sup.71 is a C.sub.1-C.sub.20 hydrocarbylene group which may contain a heteroatom, [0064] Z.sup.8 is each independently a single bond,  $\text{****—Z.sup.81—C(=O)—O—}$ ,  $\text{****—C(=O)—NH—Z.sup.81—}$ , or  $\text{****—O—Z.sup.81—}$ , Z.sup.81 is a C.sub.1-C.sub.20 hydrocarbylene group which may contain a heteroatom, [0065] Z.sup.9 is a single bond, methylene, ethylene, phenylene, fluorinated phenylene, trifluoromethyl-substituted phenylene,  $\text{*—C(=O)—O—Z.sup.91—}$ ,  $\text{*—C(=O)—N(H)—Z.sup.91—}$ , or  $\text{*—O—Z.sup.91—}$ , Z.sup.91 is a C.sub.1-C.sub.6 aliphatic hydrocarbylene group, phenylene group, fluorinated phenylene group or trifluoromethyl-substituted phenylene group, which may contain a carbonyl moiety, ester bond, ether bond or hydroxy moiety, [0066] \* designates a point of attachment to the carbon atom in the backbone, \*\* designates a point of attachment to Z.sup.1, \*\*\* designates a point of attachment to Z.sup.6, \*\*\*\* designates a point of attachment to Z.sup.7, [0067] R.sup.31 and R.sup.32 are each independently a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, R.sup.31 and R.sup.32 may bond together to form a ring with the sulfur atom to which they are attached, [0068] L.sup.1 is a single bond, ether bond, ester bond, carbonyl group, sulfonate ester bond, carbonate bond or carbamate bond, [0069] Rf.sup.1 and Rf.sup.2 are each independently fluorine or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group, [0070] Rf.sup.3 and Rf.sup.4 are each independently hydrogen, fluorine, or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group, [0071] Rf.sup.5 and Rf.sup.6 are each independently hydrogen, fluorine, or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group, excluding that all Rf.sup.5 and Rf.sup.6 are hydrogen at the same time, [0072] M.sup.– is a non-nucleophilic counter ion, [0073] A.sup.+ is an onium cation, and [0074] d is 0, 1, 2 or 3.

[0075] The resist composition may further comprise an organic solvent, a photoacid generator capable of generating a strong acid, a quencher other than the quencher of claim 6, and/or a surfactant.

[0076] In a further aspect, the invention provides a pattern forming process comprising the steps of

applying the chemically amplified resist composition defined herein onto a substrate to form a resist film thereon, exposing the resist film to high-energy radiation, and developing the exposed resist film in a developer.

[0077] Typically, the high-energy radiation is KrF excimer laser radiation, ArF excimer laser radiation, EB or EUV of wavelength 3 to 15 nm.


#### Advantageous Effects of Invention

[0078] When processed by lithography, a chemically amplified resist composition comprising the inventive onium salt as a quencher exhibits a high sensitivity, high contrast, improved lithography properties including EL, LWR, CDU and DOF.

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## Description

### DETAILED DESCRIPTION OF THE INVENTION

[0079] As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. “Optional” or “optionally” means that the subsequently described event or circumstances may or may not occur, and that description includes instances where the event or circumstance occurs and instances where it does not. The notation (C<sub>n</sub>-C<sub>m</sub>) means a group containing from n to m carbon atoms per group. In chemical formulae, the broken line () and asterisk (\*) designate a point of attachment or valence bond. Me stands for methyl and Ac for acetyl. As used herein, the term “fluorinated” refers to a fluorine-substituted or fluorine-containing compound or group, and “iodized” refers to an iodine-substituted or iodine-containing compound or group. The terms “group” and “moiety” are interchangeable.

[0080] The abbreviations and acronyms have the following meaning. [0081] EB: electron beam [0082] EUV: extreme ultraviolet [0083] Mw: weight average molecular weight [0084] Mn: number average molecular weight [0085] Mw/Mn: molecular weight distribution or dispersity [0086] GPC: gel permeation chromatography [0087] PEB: post-exposure bake [0088] PAG: photoacid generator [0089] LWR: line width roughness [0090] CDU: critical dimension uniformity [0091] EL: exposure latitude [0092] DOF: depth of focus

#### [Onium Salt]

[0093] One embodiment of the invention is an onium salt consisting of an aromatic carboxylic acid anion including a partial structure having iodine and a cyclic ether structure and an onium cation.

[0094] Preferably, the onium salt has the formula (1).

##STR00007##

[0095] In formula (1), n<sub>1</sub> is 0 or 1. The relevant structure is a benzene ring in case of n<sub>1</sub>=0, and a naphthalene ring in case of n<sub>1</sub>=1. The benzene ring corresponding to n<sub>1</sub>=0 is preferred from the standpoint of solvent solubility. The subscript n<sub>2</sub> is an integer of 1 to 4. It is preferred from the standpoint of availability of reactants that n<sub>2</sub> be 1, 2 or 3, more preferably 1 or 2. The subscript n<sub>3</sub> is an integer of 1 to 4. From the standpoint of availability of reactants, n<sub>3</sub> is preferably 1, 2 or 3, and from the standpoint of solvent solubility, n<sub>3</sub> is more preferably 1 or 2. The subscript n<sub>4</sub> is an integer of 0 to 3. These subscripts meet 2≤n<sub>2</sub>+n<sub>3</sub>+n<sub>4</sub>≤5 in case of n<sub>1</sub>=0 and 2≤n<sub>2</sub>+n<sub>3</sub>+n<sub>4</sub>≤7 in case of n<sub>1</sub>=1.

[0096] In formula (1), W<sup>sup</sup>.A is a C<sub>2</sub>-C<sub>10</sub> group containing a cyclic ether structure. The group containing a cyclic ether structure is preferably an optionally substituted oxirane ring, optionally substituted oxetane ring, optionally substituted tetrahydrofuran ring or optionally substituted tetrahydropyran ring, more preferably an optionally substituted oxirane ring or optionally substituted oxetane ring. The preferred substituent is a C<sub>1</sub>-C<sub>8</sub> saturated hydrocarbyl group, more preferably methyl or ethyl.

[0097] In formula (1), R<sup>sup</sup>.1 is halogen exclusive of iodine, or a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl group which may contain a heteroatom. Examples of the halogen exclusive of iodine include

fluorine, chlorine and bromine, with fluorine being preferred. The C.sub.1-C.sub.20 hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C.sub.1-C.sub.20 alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, tert-pentyl, n-pentyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, and n-dodecyl; C.sub.3-C.sub.20 cyclic saturated hydrocarbyl groups such as cyclopentyl, cyclohexyl, cyclopentylmethyl, cyclopentylethyl, cyclopentylbutyl, cyclohexylmethyl, cyclohexylethyl, cyclohexylbutyl, norbornyl, norbornylmethyl, adamantyl, adamantylmethyl, tricyclo[5.2.1.0<sup>sup</sup>.2,6]decyl, tetracyclo[6.2.1.1<sup>sup</sup>.3,6.0<sup>sup</sup>.2,7]dodecyl; C.sub.2-C.sub.20 alkenyl groups such as vinyl, allyl, propenyl, butenyl, pentenyl, hexenyl; C.sub.2-C.sub.20 alkynyl groups such as ethynyl, propynyl, butynyl, pentynyl, and hexynyl; C.sub.3-C.sub.20 cyclic unsaturated aliphatic hydrocarbyl groups such as cyclopentenyl and cyclohexenyl; C.sub.6-C.sub.20 aryl groups such as phenyl, naphthyl, and indanyl; C.sub.7-C.sub.20 aralkyl groups such as benzyl, 1-phenylethyl, and 2-phenylethyl, and combinations thereof. The hydrocarbyl group may contain a heteroatom such as halogen, oxygen or sulfur.

[0098] When n<sub>4</sub> is 2 or 3, a plurality of R<sup>sup</sup>.1 may bond together to form a ring with the carbon atoms on the aromatic ring to which they are attached, and some —CH<sub>2</sub>— in the ring may be replaced by —O— or —S—. Exemplary rings include cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, norbornane, adamantane, tricyclo[5.2.1.0<sup>sup</sup>.2,6]decane, and tetracyclo[6.2.1.1<sup>sup</sup>.3,6.0<sup>sup</sup>.2,7]dodecane rings as well as these rings in which some —CH<sub>2</sub>— is replaced by —O— or —S—.

[0099] In formula (1), L<sup>sup</sup>.A and L<sup>sup</sup>.B are each independently a single bond, ether bond, thioether bond, ester bond, amide bond, sulfonate ester bond, carbonate bond or carbamate bond. L<sup>sup</sup>.A is preferably a single bond, ether bond, thioether bond or ester bond, more preferably an ether bond or thioether bond. L<sup>sup</sup>.B is preferably a single bond, ether bond, thioether bond or ester bond, more preferably a single bond, ether bond or ester bond.

[0100] In formula (1), X<sup>sup</sup>.L is a single bond or a C.sub.1-C.sub.40 hydrocarbylene group which may contain a heteroatom. The hydrocarbylene group may be straight, branched or cyclic and examples thereof include alkanediyl, cyclic saturated hydrocarbylene and arylene groups. Suitable heteroatoms include oxygen, nitrogen and sulfur.

[0101] Examples of the optionally heteroatom-containing C.sub.1-C.sub.40 hydrocarbylene group X<sup>sup</sup>.L are shown below, but not limited thereto. Herein, \* designates a point of attachment to L<sup>sup</sup>.A or L<sup>sup</sup>.B.

##STR00008## ##STR00009## ##STR00010## ##STR00011## ##STR00012## ##STR00013##

[0102] Of these, X<sup>sup</sup>.L-0 to X<sup>sup</sup>.L-22 and X<sup>sup</sup>.L-47 to X<sup>sup</sup>.L-58 are preferred.

[0103] Examples of the anion in the onium salt having formula (1) are shown below, but not limited thereto.

##STR00014## ##STR00015## ##STR00016## ##STR00017## ##STR00018## ##STR00019##  
##STR00020## ##STR00021## ##STR00022## ##STR00023## ##STR00024## ##STR00025##  
##STR00026## ##STR00027## ##STR00028## ##STR00029## ##STR00030## ##STR00031##  
##STR00032## ##STR00033## ##STR00034## ##STR00035## ##STR00036## ##STR00037##  
##STR00038## ##STR00039## ##STR00040## ##STR00041## ##STR00042## ##STR00043##  
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##STR00194## ##STR00195## ##STR00196## ##STR00197## ##STR00198## ##STR00199##  
##STR00200## ##STR00201##  
##STR00202## ##STR00203## ##STR00204## ##STR00205## ##STR00206## ##STR00207##  
##STR00208##

[0104] In formula (1), Z<sup>sup.</sup>+ is an onium cation, which is preferably selected from sulfonium cations having the formula (cation-1), iodonium cations having the formula (cation-2), and ammonium cations having the formula (cation-3).

##STR00209##

[0105] In formulae (cation-1) to (cation-3), R<sup>sup.ct1</sup> to R<sup>sup.ct9</sup> are each independently halogen or a C<sub>sub.1</sub>-C<sub>sub.30</sub> hydrocarbyl group which may contain a heteroatom. Suitable halogen atoms include fluorine, chlorine, bromine and iodine. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C<sub>sub.1</sub>-C<sub>sub.30</sub> alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl; C<sub>sub.3</sub>-C<sub>sub.30</sub> cyclic saturated hydrocarbyl groups such as cyclopropyl, cyclopentyl, cyclohexyl, cyclopropylmethyl, 4-methylcyclohexyl, cyclohexylmethyl, norbornyl, adamantyl; C<sub>sub.2</sub>-C<sub>sub.30</sub> alkenyl groups such as vinyl, allyl, propenyl, butenyl, hexenyl; C<sub>sub.3</sub>-C<sub>sub.30</sub> cyclic unsaturated hydrocarbyl groups such as cyclohexenyl; C<sub>sub.6</sub>-C<sub>sub.30</sub> aryl groups such as phenyl, naphthyl, thienyl; C<sub>sub.7</sub>-C<sub>sub.30</sub> aralkyl groups such as benzyl, 1-phenylethyl, 2-phenylethyl, and combinations thereof. Inter alia, the aryl groups are preferred. In the hydrocarbyl groups, some or all hydrogen may be substituted by a moiety containing a heteroatom such as oxygen, sulfur, nitrogen or halogen, and some —CH<sub>sub.2</sub>— may be replaced by a moiety containing a heteroatom such as oxygen, sulfur or nitrogen, so that the group may contain a hydroxy, fluorine, chlorine, bromine, iodine, cyano, nitro, carbonyl, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring, carboxylic anhydride (—C(=O)—O—C(=O)—) or haloalkyl moiety.

[0106] Also, any two of R<sup>sup.ct1</sup> to R<sup>sup.ct3</sup> may bond together to form a ring with the sulfur atom to which they are attached. Exemplary structures of the ring are shown below.

##STR00210##

[0107] The broken line designates a point of attachment to R<sup>sup.ct3</sup>.

[0108] Any two of R<sup>sup.ct6</sup> to R<sup>sup.ct9</sup> may bond together to form a ring with the nitrogen atom to which they are attached.

[0109] Examples of the sulfonium cation having formula (cation-1) are shown below, but not limited thereto.



##STR00211## ##STR00212## ##STR00213## ##STR00214## ##STR00215## ##STR00216##  
##STR00217## ##STR00218## ##STR00219## ##STR00220## ##STR00221## ##STR00222##  
##STR00223## ##STR00224## ##STR00225## ##STR00226## ##STR00227## ##STR00228##  
##STR00229##  
##STR00230## ##STR00231## ##STR00232## ##STR00233## ##STR00234## ##STR00235##  
##STR00236## ##STR00237## ##STR00238## ##STR00239## ##STR00240## ##STR00241##  
##STR00242## ##STR00243## ##STR00244## ##STR00245## ##STR00246## ##STR00247##  
##STR00248## ##STR00249##  
##STR00250## ##STR00251## ##STR00252## ##STR00253## ##STR00254## ##STR00255##  
##STR00256## ##STR00257## ##STR00258## ##STR00259## ##STR00260## ##STR00261##  
##STR00262## ##STR00263## ##STR00264## ##STR00265## ##STR00266## ##STR00267##  
##STR00268## ##STR00269## ##STR00270##

[0110] Examples of the iodonium cation having formula (cation-2) are shown below, but not limited hereto.

##STR00271## ##STR00272## ##STR00273##

[0111] Examples of the ammonium cation having formula (cation-3) are shown below, but not limited thereto.

##STR00274##

[0112] Examples of the onium salt include arbitrary combinations of anions with cations, both as exemplified above.

[0113] The onium salt having formula (1) can be synthesized by well-known methods. As a typical example, a method of preparing an onium salt having formula (PDQ-1-ex) is described.

##STR00275##

[0114] Herein n1 to n4, W<sup>sup</sup>.A, R<sup>sup</sup>.1, L<sup>sup</sup>.A, X<sup>sup</sup>.L, and Z<sup>sup</sup>.+ are as defined above, R<sup>sup</sup>.X is a group which forms a primary or secondary ester with the adjacent carbonyloxy group, R<sup>sup</sup>.Y is a leaving group such as chlorine, bromine, iodine, p-toluenesulfonyl, methanesulfonyl or trifluoromethanesulfonyl group, and X<sup>sup</sup>.- is a counter anion.

[0115] The first step is to react Reactants SM-1 and SM-2, which are commercially available or can be synthesized by any well-known synthesis method, to form Intermediate In-1. The reaction may be performed by any well-known organic synthesis method. Specifically, the reaction is carried out by dissolving Reactant SM-1 in an aprotic polar solvent such as acetone, acetonitrile, dimethylsulfoxide (DMSO) or N,N-dimethylformamide (DMF), adding a base, and adding Reactant SM-2 thereto dropwise. Examples of the base used herein include hydroxides such as sodium hydroxide, potassium hydroxide, and tetramethylammonium hydroxide and carbonates such as potassium carbonate and sodium hydrogencarbonate. The bases may be used alone or in admixture. The reaction system may be heated if necessary. The reaction temperature ranges from room temperature to near the boiling point of the solvent. Heating conditions are preferred for the smooth progress of reaction. The reaction may also be accelerated by adding a catalyst such as an alkali metal iodide, e.g., sodium iodide or potassium iodide. The reaction time is determined as appropriate by monitoring the reaction process by silica gel thin-layer chromatography (TLC) because it is desirable from the yield aspect to drive the reaction to completion. Typically the reaction time is about 4 to 12 hours. Thereafter, water is added to quench the reaction. The desired compound is extracted from the reaction mixture. Through ordinary aqueous work-up, Intermediate In-1-ex is recovered. The resulting Intermediate In-1 may be purified by a standard technique such as chromatography or re-crystallization if necessary.

[0116] The second step is to produce onium salt PDQ-1-ex through hydrolysis of the primary or secondary ester bond: —CO<sub>2</sub>R<sup>sup</sup>.X in Intermediate In-1-ex with a base, and subsequent salt exchange with an onium salt Z<sup>sup</sup>.+X<sup>sup</sup>-. The reaction may be performed by any well-known organic synthesis method. Specifically, the alkaline hydrolysis step is carried out by suspending Intermediate In-1-ex in water or an ether solvent such as tetrahydrofuran (THF), and adding a base

thereto. As the base, an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide is preferred. The reaction temperature ranges from room temperature to near the boiling point of the solvent. Heating conditions are preferred for the smooth progress of reaction. The reaction time is determined as appropriate by monitoring the reaction process by TLC because it is desirable from the yield aspect to drive the reaction to completion. Typically the reaction time is about 4 to 12 hours. Although the hydrolysate may be isolated from the reaction solution, it is preferred that the reaction solution be directly subjected to a salt exchange with an onium salt  $Z.sup.+X.sup.-$ , i.e., without isolation. The salt exchange reaction is carried out by adding a solvent such as methylene chloride to the solution after alkaline hydrolysis and stirring the two-layer system. As the counter anion  $X-$ , chloride, bromide, iodide and methylsulfate anions are preferred for the quantitative progress of exchange reaction. It is preferred in view of yield to monitor the reaction process by TLC. Through ordinary aqueous work-up from the reaction mixture, Onium salt PDQ-1-ex is recovered. The resulting onium salt may be purified by a standard technique such as chromatography or re-crystallization if necessary.

[0117] The above-mentioned preparation method is merely exemplary and the method of preparing the inventive onium salt is not limited thereto.

[0118] The inventive onium salt is structurally characterized in that the aromatic carboxylic acid anion possesses a partial structure having iodine and a cyclic ether structure. Iodine is so absorptive to EUV of wavelength 13.5 nm as to generate secondary electrons upon EUV exposure, after which the energy of secondary electrons is transferred to a PAG to promote the decomposition thereof, leading to a higher sensitivity. In addition, iodine has an appropriate dissolution inhibitory ability and is thus effective for restraining the pattern in the unexposed region from collapse in alkaline developer. On the other hand, the cyclic ether structure functions as an acid diffusion suppressing group in that the hydrogen bond formed between the ether oxygen atom and the acid generated from the PAG acts to suppress excessive acid diffusion. Since the inventive onium salt has the aromatic carboxylic acid anion, it has a relatively strong basicity enough to trap the strong acid generated from the PAG. Due to the synergy of these effects, a chemically amplified resist composition comprising the inventive onium salt exhibits a high dissolution contrast and can form line patterns with reduced LWR and hole patterns with improved CDU, both the patterns having collapse resistance. The onium salt is thus useful as one component of a chemically amplified resist composition, especially of positive tone.

[0119] The inventive onium salt is advantageously used as a quencher. As used herein, the term “quencher” refers to a compound capable of trapping the strong acid generated by a PAG in the resist composition to prevent the acid from diffusing to the unexposed region and to assist in forming the desired pattern. As used herein, the “PAG” refers to a compound capable of generating a strong acid upon exposure to high-energy radiation, and the term “strong acid” refers to a compound having a sufficient acidity to induce deprotection reaction of an acid labile group. Since the aromatic carboxylic acid does not have an enough acidity to induce deprotection reaction of an acid labile group which is tertiary ester or tertiary ether, it is effective to separately add a PAG capable of generating a strong acid, i.e.,  $\alpha$ -fluorinated sulfonic acid, imide acid or methide acid, for the purpose of inducing deprotection reaction of an acid labile group, as will be described later. It is noted that the PAG capable of generating an  $\alpha$ -fluorinated sulfonic acid, imide acid or methide acid may be of addition type or of polymer-bound type wherein the PAG is bound to a base polymer.

[0120] In a system where the inventive onium salt capable of generating an aromatic carboxylic acid and a PAG capable of generating a ultra-strong acid or perfluoroalkylsulfonic acid are co-present, the aromatic carboxylic acid and the perfluoroalkylsulfonic acid generate upon light exposure. Since the PAG is not decomposed in its entirety, some PAG remains undecomposed nearby. If the onium salt capable of generating an aromatic carboxylic acid and perfluoroalkylsulfonic acid are co-present at this point of time, first an ion exchange occurs between the perfluoroalkylsulfonic acid and the onium salt capable of generating an aromatic

carboxylic acid whereby an onium salt of perfluoroalkylsulfonic acid is generated and the aromatic carboxylic acid is released. This is because the perfluoroalkylsulfonic acid salt having a high acid strength is more stable. On the other hand, where the perfluoroalkylsulfonic acid onium salt and the aromatic carboxylic acid are co-present, no ion exchange occurs. Similar ion exchange takes place not only with the perfluoroalkylsulfonic acid, but also with an arene sulfonic acid, alkyl sulfonic acid, imide acid or methide acid having a higher acid strength than the aromatic carboxylic acid generated by the inventive onium salt.

[Chemically Amplified Resist Composition]

(A) Quencher

[0121] Another embodiment of the invention is a chemically amplified resist composition essentially comprising (A) a quencher in the form of the onium salt having formula (1).

[0122] In the chemically amplified resist composition, the amount of quencher (A) is preferably 0.1 to 40 parts by weight, more preferably 0.5 to 30 parts by weight per 80 parts by weight of a base polymer to be described just below. As long as the amount of quencher (A) is in the range, good sensitivity and resolution are achievable and the risk of foreign particles being formed after development or during stripping of resist film is avoided. The quencher may be used alone or in admixture.

(B) Base Polymer

[0123] The chemically amplified resist composition may comprise a base polymer as component (B). The base polymer (B) contains repeat units having the formula (a1), which are also referred to as repeat units (a1).

##STR00276##

[0124] In formula (a1), R.sup.A is hydrogen, fluorine, methyl or trifluoromethyl.

[0125] In formula (a1), X.sup.1 is a single bond, phenylene group, naphthylene group or \*—C(=O)—O—X.sup.11—. The phenylene or naphthylene group may be substituted with an optionally fluorinated C.sub.1-C.sub.10 alkoxy moiety or halogen. X.sup.11 is a C.sub.1-C.sub.10 saturated hydrocarbylene group, phenylene or naphthylene group, and the saturated hydrocarbylene group may contain a hydroxy moiety, ether bond, ester bond or lactone ring. The asterisk (\*) designates a point of attachment to the carbon atom in the backbone.

[0126] In formula (a1), AL.sup.1 is an acid labile group. Examples of the acid labile group include those described in U.S. Pat. No. 8,574,817 (JP-A 2013-080033) and U.S. Pat. No. 8,846,303 (JP-A 2013-083821).

[0127] Typical of the acid labile group are groups of the following formulae (AL-1) to (AL-3).

##STR00277##

[0128] In formulae (AL-1) and (AL-2), R.sup.L1 and R.sup.L2 are each independently a C.sub.1-C.sub.40 hydrocarbyl group which may contain a heteroatom such as oxygen, sulfur, nitrogen or fluorine. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Inter alia, C.sub.1-C.sub.20 hydrocarbyl groups are preferred.

[0129] In formula (AL-1), k is an integer of 0 to 10, preferably 1 to 5.

[0130] In formula (AL-2), R.sup.L3 and R.sup.L4 are each independently hydrogen or a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom such as oxygen, sulfur, nitrogen or fluorine. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Any two of R.sup.L2, R.sup.L3 and R.sup.L4 may bond together to form a C.sub.3-C.sub.20 ring with the carbon atom or carbon and oxygen atoms to which they are attached. The ring preferably contains 4 to 16 carbon atoms and is typically alicyclic.

[0131] In formula (AL-3), R.sup.L5, R.sup.L6 and R.sup.L7 are each independently a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom such as oxygen, sulfur, nitrogen or fluorine. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Any two of R.sup.L5, R.sup.L6 and R.sup.L7 may bond together to form a C.sub.3-C.sub.20 ring with the carbon atom to which they are attached. The ring preferably contains 4 to 16 carbon atoms

and is typically alicyclic.

[0132] Examples of repeat unit (a1) are shown below, but not limited thereto. Herein R.sup.A and AL.sup.1 are as defined above.

##STR00278## ##STR00279## ##STR00280## ##STR00281## ##STR00282## ##STR00283##

[0133] The base polymer (B) may further contain repeat units having the formula (a2), which are also referred to as repeat units (a2).

##STR00284##

[0134] In formula (a2), R.sup.A is hydrogen, fluorine, methyl or trifluoromethyl. X.sup.2 is a single bond or  $\text{*—C(=O)—O—}$  wherein \* designates a point of attachment to the carbon atom in the backbone. R.sup.11 is halogen, cyano, a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, a C.sub.1-C.sub.20 hydrocarbyloxy group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyl group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyloxy group which may contain a heteroatom, or a C.sub.2-C.sub.20 hydrocarbyloxycarbonyl group which may contain a heteroatom. AL.sup.2 is an acid labile group, examples of which are as exemplified for the acid labile group AL.sup.1. The subscript “a” is an integer of 0 to 4, preferably 0 or 1.

[0135] Examples of the repeat unit (a2) are shown below, but not limited thereto. Herein R.sup.A and AL.sup.2 are as defined above.

##STR00285## ##STR00286## ##STR00287## ##STR00288##

[0136] In a preferred embodiment, the base polymer further comprises repeat units having the formula (b1) or repeat units having the formula (b2), which are simply referred to as repeat units (b1) or (b2).

##STR00289##

[0137] In formulae (b1) and (b2), R.sup.A is each independently hydrogen, fluorine, methyl or trifluoromethyl. Y.sup.1 is a single bond or  $\text{*—C(=O)—O—}$  wherein \* designates a point of attachment to the carbon atom in the backbone. R.sup.21 is hydrogen or a C.sub.1-C.sub.20 group containing at least one structure selected from among hydroxy other than phenolic hydroxy, cyano, carbonyl, carboxy, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring and carboxylic anhydride ( $\text{—C(=O)—O—C(=O)—}$ ). R.sup.22 is halogen, hydroxy, carboxy, nitro, cyano, a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, C.sub.1-C.sub.20 hydrocarbyloxy group which may contain a heteroatom, C.sub.2-C.sub.20 hydrocarbylcarbonyl group which may contain a heteroatom, C.sub.2-C.sub.20 hydrocarbylcarbonyloxy group which may contain a heteroatom or C.sub.2-C.sub.20 hydrocarbyloxycarbonyl group which may contain a heteroatom. The subscript b is an integer of 1 to 4, c is an integer of 0 to 4, and b+c is from 1 to 5.

[0138] Examples of the repeat unit (b1) are shown below, but not limited thereto. Herein, R.sup.A is as defined above.

##STR00290## ##STR00291## ##STR00292## ##STR00293## ##STR00294## ##STR00295##  
##STR00296## ##STR00297## ##STR00298## ##STR00299## ##STR00300## ##STR00301##  
##STR00302## ##STR00303## ##STR00304## ##STR00305## ##STR00306##  
##STR00307## ##STR00308## ##STR00309## ##STR00310## ##STR00311## ##STR00312##  
##STR00313## ##STR00314## ##STR00315## ##STR00316## ##STR00317## ##STR00318##  
##STR00319## ##STR00320## ##STR00321## ##STR00322## ##STR00323##

[0139] Examples of the repeat unit (b2) are shown below, but not limited thereto. Herein, R.sup.A is as defined above.

##STR00324## ##STR00325## ##STR00326## ##STR00327## ##STR00328## ##STR00329##  
##STR00330## ##STR00331## ##STR00332## ##STR00333## ##STR00334##

[0140] Of the repeat units (b1) and (b2), those units having a lactone ring as the polar group are preferred in the ArF lithography and those units having a phenolic site are preferred in the KrF, EB and EUV lithography.

[0141] The base polymer may further comprise repeat units of at least one type selected from repeat units having the formulae (c1) to (c4), which are simply referred to as repeat units (c1) to (c4).

##STR00335##

[0142] In formulae (c1) to (c4), R<sup>sup</sup>.A is each independently hydrogen, fluorine, methyl or trifluoromethyl. Z<sup>sup</sup>.1 is a single bond or optionally substituted phenylene group. Z<sup>sup</sup>.2 is a single bond,  $**\text{—C(=O)—O—Z}^{\text{sup}}.21\text{—}$ ,  $**\text{—C(=O)—N(H)—Z}^{\text{sup}}.21\text{—}$  or  $**\text{—O—Z}^{\text{sup}}.21\text{—}$ . Z<sup>sup</sup>.21 is a C<sub>sub</sub>.1-C<sub>sub</sub>.6 aliphatic hydrocarbylene group, a phenylene group or a divalent group obtained by combining the foregoing, which may contain halogen, carbonyl moiety, ester bond, ether bond or hydroxy moiety. Z<sup>sup</sup>.3 is a single bond, ether bond, ester bond, amide bond, sulfonate ester bond, sulfonamide bond, carbonate bond or carbamate bond. Z<sup>sup</sup>.4 is a single bond, or a C<sub>sub</sub>.1-C<sub>sub</sub>.6 aliphatic hydrocarbylene group, phenylene group or a divalent group obtained by combining the foregoing, which may contain halogen, carbonyl moiety, ester bond, ether bond or hydroxy moiety. Z<sup>sup</sup>.5 is each independently a single bond, optionally substituted phenylene group, naphthylene group, or  $*\text{—C(=O)—O—Z}^{\text{sup}}.51\text{—}$ . Z<sup>sup</sup>.51 is a C<sub>sub</sub>.1-C<sub>sub</sub>.10 aliphatic hydrocarbylene group which may contain halogen, hydroxy moiety, ether bond, ester bond or lactone ring, or phenylene or naphthylene group. Z<sup>sup</sup>.6 is a single bond, ether bond, ester bond, amide bond, sulfonate ester bond, sulfonic amide bond, carbonate bond or carbamate bond. Z<sup>sup</sup>.7 is each independently a single bond,  $***\text{—Z}^{\text{sup}}.71\text{—C(=O)—O—}$ ,  $***\text{—C(=O)—NH—Z}^{\text{sup}}.71\text{—}$ , or  $***\text{—O—Z}^{\text{sup}}.71\text{—}$ . Z<sup>sup</sup>.71 is a C<sub>sub</sub>.1-C<sub>sub</sub>.20 hydrocarbylene group which may contain a heteroatom. Z<sup>sup</sup>.8 is each independently a single bond,  $****\text{—Z}^{\text{sup}}.81\text{—C(=O)—O—}$ ,  $****\text{—C(=O)—NH—Z}^{\text{sup}}.81\text{—}$ , or  $****\text{—O—Z}^{\text{sup}}.81\text{—}$ . Z<sup>sup</sup>.81 is a C<sub>sub</sub>.1-C<sub>sub</sub>.20 hydrocarbylene group which may contain a heteroatom. Z<sup>sup</sup>.9 is a single bond, methylene, ethylene, phenylene, fluorinated phenylene, trifluoromethyl-substituted phenylene,  $*\text{—C(=O)—O—Z}^{\text{sup}}.91\text{—}$ ,  $*\text{—C(=O)—N(H)—Z}^{\text{sup}}.91\text{—}$ , or  $*\text{—O—Z}^{\text{sup}}.91\text{—}$ . Z<sup>sup</sup>.91 is a C<sub>sub</sub>.1-C<sub>sub</sub>.6 aliphatic hydrocarbylene group, phenylene group, fluorinated phenylene group or trifluoromethyl-substituted phenylene group, which may contain a carbonyl moiety, ester bond, ether bond or hydroxy moiety. The asterisk \* designates a point of attachment to the carbon atom in the backbone, \*\* designates a point of attachment to Z<sup>sup</sup>.1, \*\*\* designates a point of attachment to Z<sup>sup</sup>.6, and \*\*\*\* designates a point of attachment to Z<sup>sup</sup>.7.

[0143] The aliphatic hydrocarbylene group represented by Z<sup>sup</sup>.21, Z<sup>sup</sup>.51 and Z<sup>sup</sup>.91 may be straight, branched or cyclic. Examples thereof include alkanediyl groups such as methanediyl, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, propane-2,2-diyl, butane-1,1-diyl, butane-1,2-diyl, butane-1,3-diyl, butane-2,3-diyl, butane-1,4-diyl, 1,1-dimethylethane-1,2-diyl, pentane-1,5-diyl, 2-methylbutane-1,2-diyl, and hexane-1,6-diyl; cycloalkanediyl groups such as cyclopropanediyl, cyclobutanediyl, cyclopentanedil and cyclohexanedil, and combinations thereof.

[0144] The hydrocarbylene group which may contain a heteroatom, represented by Z<sup>sup</sup>.71 and Z<sup>sup</sup>.81, may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are shown below, but not limited thereto.

##STR00336##

[0145] In formula (c1), R<sup>sup</sup>.31 and R<sup>sup</sup>.32 are each independently a C<sub>sub</sub>.1-C<sub>sub</sub>.20 hydrocarbyl group which may contain a heteroatom. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C<sub>sub</sub>.1-C<sub>sub</sub>.20 alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl; C<sub>sub</sub>.3-C<sub>sub</sub>.20 cyclic saturated hydrocarbyl groups such as cyclopropyl, cyclopentyl, cyclohexyl, cyclopropylmethyl, 4-methylcyclohexyl, cyclohexylmethyl, norbornyl, and adamantyl; C<sub>sub</sub>.2-C<sub>sub</sub>.20 alkenyl groups such as vinyl, allyl, propenyl, butenyl, and hexenyl; C<sub>sub</sub>.3-C<sub>sub</sub>.20 cyclic unsaturated hydrocarbyl groups such as cyclohexenyl; C<sub>sub</sub>.6-C<sub>sub</sub>.20 aryl groups such as phenyl, naphthyl and thienyl; C<sub>sub</sub>.7-C<sub>sub</sub>.20 aralkyl groups such as benzyl, 1-

phenylethyl, and 2-phenylethyl, and combinations thereof. Of these, aryl groups are preferred. In the hydrocarbyl group, some or all hydrogen may be substituted by a moiety containing a heteroatom such as oxygen, sulfur, nitrogen or halogen, and some —CH<sub>2</sub>— may be replaced by a moiety containing a heteroatom such as oxygen, sulfur or nitrogen, so that the group may contain a hydroxy, fluorine, chlorine, bromine, iodine, cyano, carbonyl, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring, carboxylic anhydride (—C(=O)—O—C(=O)—) or haloalkyl moiety.

[0146] R<sup>sup</sup>.31 and R<sup>sup</sup>.32 may bond together to form a ring with the sulfur atom to which they are attached. Examples of the ring are as exemplified above for the ring that R<sup>sup</sup>.ct1 and R<sup>sup</sup>.ct2 in formula (cation-1) form with the sulfur atom to which they are attached.

[0147] Examples of the cation in repeat unit (c1) are given below, but not limited thereto. Herein R<sup>sup</sup>.A is as defined above.

##STR00337## ##STR00338## ##STR00339## ##STR00340## ##STR00341## ##STR00342##  
##STR00343## ##STR00344## ##STR00345## ##STR00346## ##STR00347## ##STR00348##  
##STR00349## ##STR00350## ##STR00351## ##STR00352## ##STR00353## ##STR00354##  
##STR00355## ##STR00356## ##STR00357## ##STR00358## ##STR00359## ##STR00360##  
##STR00361## ##STR00362## ##STR00363##

[0148] In formula (c1), M<sup>sup</sup>.- is a non-nucleophilic counter ion. Halide, sulfonate, imide and methide anions are preferred. Examples of the non-nucleophilic counter ion include halide ions such as chloride and bromide ions; sulfonate anions, specifically fluoroalkylsulfonate ions such as triflate, 1,1,1-trifluoroethanesulfonate, and nonafluorobutanesulfonate, arylsulfonate ions such as tosylate, benzenesulfonate, 4-fluorobenzenesulfonate, and 1,2,3,4,5-pentafluorobenzenesulfonate, alkylsulfonate ions such as mesylate and butanesulfonate; imide ions such as bis(trifluoromethylsulfonyl)imide, bis(perfluoroethylsulfonyl)imide and bis(perfluorobutylsulfonyl)imide; and methide ions such as tris(trifluoromethylsulfonyl)methide and tris(perfluoroethylsulfonyl)methide.

[0149] Anions having the following formulae (c1-1) to (c1-4) are also useful as the non-nucleophilic counter ion.

##STR00364##

[0150] In formula (c1-1), R<sup>sup</sup>.fa is fluorine or a C<sub>1</sub>-C<sub>40</sub> hydrocarbyl group which may contain a heteroatom. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are as will be exemplified below for the hydrocarbyl group R<sup>sup</sup>.fa1 in formula (c1-1-1).

[0151] Of the anions of formula (c1-1), an anion having the formula (c1-1-1) is preferred.

##STR00365##

[0152] In formula (c1-1-1), Q<sup>sup</sup>.1 and Q<sup>sup</sup>.2 are each independently hydrogen, fluorine or a C<sub>1</sub>-C<sub>6</sub> fluorinated saturated hydrocarbyl group. It is preferred for solvent solubility that at least one of Q<sup>sup</sup>.1 and Q<sup>sup</sup>.2 be trifluoromethyl. The subscript m is an integer of 0 to 4, most preferably 1.

[0153] R<sup>sup</sup>.fa1 is a C<sub>1</sub>-C<sub>35</sub> hydrocarbyl group which may contain a heteroatom. As the heteroatom, oxygen, nitrogen, sulfur and halogen atoms are preferred, with oxygen being most preferred. Of the hydrocarbyl groups, those groups of 6 to 30 carbon atoms are preferred from the aspect of achieving a high resolution in forming patterns of small feature size. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C<sub>1</sub>-C<sub>35</sub> alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, 2-ethylhexyl, nonyl, undecyl, tridecyl, pentadecyl, heptadecyl, and icosyl; C<sub>3</sub>-C<sub>35</sub> cyclic saturated hydrocarbyl groups such as cyclopentyl, cyclohexyl, 1-adamantyl, 2-adamantyl, 1-adamantylmethyl, norbornyl, norbornylmethyl, tricyclodecyl, tetracyclododecyl, tetracyclododecylmethyl, and dicyclohexylmethyl; C<sub>2</sub>-C<sub>35</sub> unsaturated aliphatic hydrocarbyl groups such as allyl and

3-cyclohexenyl; C.sub.6-C.sub.35 aryl groups such as phenyl, 1-naphthyl, 2-naphthyl and 9-fluorenyl; and C.sub.7-C.sub.35 aralkyl groups such as benzyl and diphenylmethyl, and combinations thereof.

[0154] In the foregoing hydrocarbyl groups, some or all hydrogen may be substituted by a moiety containing a heteroatom such as oxygen, sulfur, nitrogen or halogen, or some constituent — CH.sub.2 — may be replaced by a moiety containing a heteroatom such as oxygen, sulfur or nitrogen, so that the group may contain a hydroxy, fluorine, chlorine, bromine, iodine, cyano, nitro, carbonyl, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring, carboxylic anhydride ( $\text{—C(=O)—O—C(=O)—}$ ) or haloalkyl moiety. Examples of the heteroatom-containing hydrocarbyl group include tetrahydrofuryl, methoxymethyl, ethoxymethyl, methylthiomethyl, acetamidomethyl, trifluoroethyl, (2-methoxyethoxy)methyl, acetoxymethyl, 2-carboxy-1-cyclohexyl, 2-oxopropyl, 4-oxo-1-adamantyl, and 3-oxocyclohexyl.

[0155] In formula (c1-1-1), L.sup.1 is a single bond, ether bond, ester bond, sulfonate ester bond, carbonate bond or carbamate bond. From the aspect of synthesis, an ether bond or ester bond is preferred, with the ester bond being more preferred.

[0156] Examples of the anion having formula (c1-1) are shown below, but not limited thereto. Herein Q.sup.1 is as defined above.

##STR00366## ##STR00367## ##STR00368## ##STR00369## ##STR00370## ##STR00371##  
##STR00372## ##STR00373## ##STR00374## ##STR00375## ##STR00376## ##STR00377##  
##STR00378##

[0157] In formula (c1-2), R.sup.fb1 and R.sup.fb2 are each independently fluorine or a C.sub.1-C.sub.40 hydrocarbyl group which may contain a heteroatom. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are as exemplified above for the hydrocarbyl group R.sup.fa1 in formula (c1-1-1). Preferably R.sup.fb1 and R.sup.fb2 are fluorine or C.sub.1-C.sub.4 straight fluorinated alkyl groups. Also, R.sup.fb1 and R.sup.fb2 may bond together to form a ring with the linkage:  $\text{—CF.sub.2—SO.sub.2—N—SO.sub.2—CF.sub.2—}$  to which they are attached. It is preferred that a combination of R.sup.fb1 and R.sup.fb2 be a fluorinated ethylene or fluorinated propylene group.

[0158] In formula (c1-3), R.sup.fc1, R.sup.fc2 and R.sup.fc3 are each independently fluorine or a C.sub.1-C.sub.40 hydrocarbyl group which may contain a heteroatom. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are as exemplified above for the hydrocarbyl group R.sup.fa1 in formula (c1-1-1). Preferably R.sup.fc1, R.sup.fc2 and R.sup.fc3 are fluorine or C.sub.1-C.sub.4 straight fluorinated alkyl groups. Also, R.sup.fc1 and R.sup.fc2 may bond together to form a ring with the linkage:  $\text{—CF.sub.2—SO.sub.2—C—SO.sub.2—CF.sub.2—}$  to which they are attached. It is preferred that a combination of R.sup.fc1 and R.sup.fc2 be a fluorinated ethylene or fluorinated propylene group.

[0159] In formula (c1-4), R.sup.fd is a C.sub.1-C.sub.40 hydrocarbyl group which may contain a heteroatom. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are as exemplified above for R.sup.fa1.

[0160] Examples of the anion having formula (c1-4) are shown below, but not limited thereto.

##STR00379## ##STR00380##  
[0161] Anions having an iodized or brominated aromatic ring are also useful as the non-nucleophilic counter ion. These anions have the formula (c1-5).

##STR00381##  
[0162] In formula (c1-5), x is an integer of 1 to 3, y is an integer of 1 to 5, z is an integer of 0 to 3, and y+z is from 1 to 5. Preferably, y is 1, 2 or 3, more preferably 2 or 3, and z is 0, 1 or 2.

[0163] X.sup.BI is iodine or bromine. A plurality of X.sup.BI may be identical or different when x and/or y is 2 or more.

[0164] L.sup.1 is a single bond, ether bond, ester bond, or a C.sub.1-C.sub.6 saturated hydrocarbylene group which may contain an ether bond or ester bond. The saturated

hydrocarbylene group may be straight, branched or cyclic.

[0165] L.sup.2 is a single bond or a C.sub.1-C.sub.20 divalent linking group when x=1, or a C.sub.1-C.sub.20 (x+1)-valent linking group when x=2 or 3. The linking group may contain an oxygen, sulfur or nitrogen atom.

[0166] R.sup.fe is hydroxy, carboxy, fluorine, chlorine, bromine, amino group, or a C.sub.1-C.sub.20 hydrocarbyl, C.sub.1-C.sub.20 hydrocarbyloxy, C.sub.2-C.sub.20 hydrocarbylcarbonyl, C.sub.2-C.sub.20 hydrocarbyloxycarbonyl, C.sub.2-C.sub.20 hydrocarbylcarbonyloxy, or C.sub.1-C.sub.20 hydrocarbylsulfonyloxy group, which may contain fluorine, chlorine, bromine, hydroxy, amino or ether bond, or —N(R.sup.feA)(R.sup.feB), —N(R.sup.feC)—C(=O)—R.sup.feD or N(R.sup.feC)—C(=O)—O—R.sup.feD. R.sup.feA and R.sup.feB are each independently hydrogen or a C.sub.1-C.sub.6 saturated hydrocarbyl group. R.sup.feC is hydrogen, or a C.sub.1-C.sub.6 saturated hydrocarbyl group which may contain halogen, hydroxy, C.sub.1-C.sub.6 saturated hydrocarbyloxy, C.sub.2-C.sub.6 saturated hydrocarbylcarbonyl or C.sub.2-C.sub.6 saturated hydrocarbylcarbonyloxy moiety. R.sup.feD is a C.sub.1-C.sub.6 aliphatic hydrocarbyl group, C.sub.6-C.sub.12 aryl group or C.sub.7-C.sub.15 aralkyl group, which may contain halogen, hydroxy, C.sub.1-C.sub.6 saturated hydrocarbyloxy, C.sub.2-C.sub.6 saturated hydrocarbylcarbonyl or C.sub.2-C.sub.6 saturated hydrocarbylcarbonyloxy moiety. The aliphatic hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. The hydrocarbyl, hydrocarbyloxy, hydrocarbylcarbonyl, hydrocarbyloxycarbonyl, hydrocarbylcarbonyloxy, and hydrocarbylsulfonyloxy groups may be straight, branched or cyclic. A plurality of R.sup.fe may be identical or different when x and/or z is 2 or more.

[0167] Of these, R.sup.fe is preferably hydroxy, —N(R.sup.feC)—C(=O)—R.sup.feD, N(R.sup.feC)C(=O)—O—R.sup.feD, fluorine, chlorine, bromine, methyl or methoxy.

[0168] Rf.sup.11 to Rf.sup.14 are each independently hydrogen, fluorine or trifluoromethyl, at least one of Rf.sup.11 to Rf.sup.14 is fluorine or trifluoromethyl. Rf.sup.11 and Rf.sup.12, taken together, may form a carbonyl group. More preferably, both Rf.sup.13 and Rf.sup.14 are fluorine.

[0169] Examples of the anion having formula (c1-5) are shown below, but not limited thereto. X.sup.BI is as defined above.

##STR00382## ##STR00383## ##STR00384## ##STR00385## ##STR00386## ##STR00387##  
##STR00388## ##STR00389## ##STR00390## ##STR00391## ##STR00392## ##STR00393##  
##STR00394## ##STR00395## ##STR00396## ##STR00397## ##STR00398## ##STR00399##  
##STR00400## ##STR00401## ##STR00402## ##STR00403## ##STR00404##  
##STR00405## ##STR00406## ##STR00407## ##STR00408## ##STR00409## ##STR00410##  
##STR00411## ##STR00412## ##STR00413## ##STR00414## ##STR00415## ##STR00416##  
##STR00417## ##STR00418## ##STR00419## ##STR00420## ##STR00421## ##STR00422##  
##STR00423## ##STR00424##  
##STR00425## ##STR00426## ##STR00427## ##STR00428## ##STR00429## ##STR00430##  
##STR00431## ##STR00432## ##STR00433## ##STR00434## ##STR00435## ##STR00436##  
##STR00437## ##STR00438## ##STR00439## ##STR00440##  
##STR00441## ##STR00442## ##STR00443## ##STR00444## ##STR00445## ##STR00446##  
##STR00447##

[0170] Other useful examples of the non-nucleophilic counter ion include fluorobenzenesulfonic acid anions having an iodized aromatic ring bonded thereto as described in JP 6648726, anions having an acid-catalyzed decomposition mechanism as described in WO 2021/200056 and JP-A 2021-070692, anions having a cyclic ether group as described in JP-A 2018-180525 and JP-A 2021-035935, and anions as described in JP-A 2018-092159.

[0171] Further useful examples of the non-nucleophilic counter ion include bulky fluorine-free benzenesulfonic acid anions as described in JP-A 2006-276759, JP-A 2015-117200, JP-A 2016-065016, and JP-A 2019-202974; fluorine-free benzenesulfonic acid or alkylsulfonic acid anions having an iodized aromatic group bonded thereto as described in JP 6645464.



[0172] Also useful are bisulfonic acid anions as described in JP-A 2015-206932, sulfonamide or sulfonimide anions having sulfonic acid side and different side as described in WO 2020/158366, and anions having a sulfonic acid side and a carboxylic acid side as described in JP-A 2015-024989.

[0173] In formulae (c2) and (c3), L.sup.1 is a single bond, ether bond, ester bond, carbonyl, sulfonate ester bond, carbonate bond or carbamate bond. From the aspect of synthesis, an ether bond, ester bond or carbonyl group is preferred, with the ester bond or carbonyl being more preferred.

[0174] In formula (c2), Rf.sup.1 and Rf.sup.2 are each independently fluorine or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group. It is preferred that both Rf.sup.1 and Rf.sup.2 be fluorine because the generated acid has a higher acid strength. Rf.sup.3 and Rf.sup.4 are each independently hydrogen, fluorine or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group. It is preferred for solvent solubility that at least one of Rf.sup.3 and Rf.sup.4 be trifluoromethyl.

[0175] In formula (c3), Rf.sup.5 and Rf.sup.6 are each independently hydrogen, fluorine or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group. It is excluded that all Rf.sup.5 and Rf.sup.6 are hydrogen at the same time. It is preferred for solvent solubility that at least one of Rf.sup.5 and Rf.sup.6 be trifluoromethyl.

[0176] In formulae (c2) and (c3), d is 0, 1, 2 or 3, preferably 1.

[0177] Examples of the anion in repeat unit (c2) are shown below, but not limited thereto. R.sup.A is as defined above.

##STR00448## ##STR00449## ##STR00450## ##STR00451## ##STR00452## ##STR00453##  
##STR00454## ##STR00455## ##STR00456## ##STR00457## ##STR00458## ##STR00459##  
##STR00460## ##STR00461## ##STR00462## ##STR00463## ##STR00464## ##STR00465##  
##STR00466## ##STR00467## ##STR00468## ##STR00469## ##STR00470## ##STR00471##  
##STR00472##

[0178] Examples of the anion in repeat unit (6) are shown below, but not limited thereto. R.sup.A is as defined above.

##STR00473## ##STR00474## ##STR00475## ##STR00476## ##STR00477## ##STR00478##  
##STR00479## ##STR00480## ##STR00481## ##STR00482## ##STR00483## ##STR00484##  
##STR00485## ##STR00486## ##STR00487## ##STR00488## ##STR00489## ##STR00490##  
##STR00491## ##STR00492## ##STR00493## ##STR00494## ##STR00495## ##STR00496##  
##STR00497## ##STR00498## ##STR00499##

[0179] Examples of the anion in repeat unit (c4) are shown below, but not limited thereto. R.sup.A is as defined above.

##STR00500## ##STR00501##

[0180] In formulae (c2) to (c4), A.sup.+ is an onium cation. Suitable onium cations include ammonium, sulfonium and iodonium cations, with the sulfonium and iodonium cations being preferred. Examples thereof are as exemplified above for the sulfonium cation having formula (cation-1), the iodonium cation having formula (cation-2) and the ammonium cation having formula (cation-3).

[0181] Exemplary structures of the repeat units (c1) to (c4) include arbitrary combinations of anions with cations, both as exemplified above.

[0182] Of the repeat units (c1) to (c4), repeat units (c2), (c3) and (c4) are preferred from the aspect of controlling acid diffusion. Repeat units (c2) and (c4) are more preferred from the aspect of the acid strength of generated acid. Repeat units (c2) are most preferred from the aspect of solvent solubility.

[0183] The base polymer may further comprise repeat units (d) of a structure having a hydroxy group protected with an acid labile group. The repeat unit (d) is not particularly limited as long as the unit includes one or more structures having a hydroxy group protected with a protective group such that the protective group is decomposed to generate the hydroxy group under the action of

acid. Repeat units having the formula (d1) are preferred.

##STR00502##

[0184] In formula (d1), R<sup>sup</sup>.A is as defined above. R<sup>sup</sup>.41 is a C<sub>sub</sub>.1-C<sub>sub</sub>.30 (e+1)-valent hydrocarbon group which may contain a heteroatom. R<sup>sup</sup>.42 is an acid labile group, and e is an integer of 1 to 4.

[0185] In formula (d1), the acid labile group R<sup>sup</sup>.42 is deprotected under the action of acid so that a hydroxy group is generated. The structure of R<sup>sup</sup>.42 is not particularly limited. An acetal structure, ketal structure, alkoxycarbonyl group and alkoxymethyl group having the following formula (d2) are preferred, with the alkoxymethyl group having formula (d2) being more preferred.

##STR00503##

[0186] Herein R<sup>sup</sup>.43 is a C<sub>sub</sub>.1-C<sub>sub</sub>.15 hydrocarbonyl group.

[0187] Illustrative examples of the acid labile group R<sup>sup</sup>.42, the alkoxymethyl group having formula (d2), and the repeat units (d) are as exemplified for the repeat units (d) in JP-A 2020-111564 (US 20200223796).

[0188] In addition to the foregoing units, the base polymer may further comprise repeat units (e) derived from indene, benzofuran, benzothiophene, acenaphthylene, chromone, coumarin, norbornadiene and derivatives thereof. Examples of the monomer from which repeat units (e) are derived are shown below, but not limited thereto.

##STR00504##

[0189] The base polymer may further comprise repeat units (f) derived from indane, vinylpyridine or vinylcarbazole.

[0190] In the polymer, repeat units (a1), (a2), (b1), (b2), (c1) to (c4), (d), (e), and (f) are incorporated in a ratio of preferably  $0 < a1 \leq 0.8$ ,  $0 \leq a2 \leq 0.8$ ,  $0 \leq b1 \leq 0.6$ ,  $0 \leq b2 \leq 0.6$ ,  $0 \leq c1 \leq 0.4$ ,  $0 \leq c2 \leq 0.4$ ,  $0 \leq c3 \leq 0.4$ ,  $0 \leq c4 \leq 0.4$ ,  $0 \leq d \leq 0.5$ ,  $0 \leq e \leq 0.3$ , and  $0 \leq f \leq 0.3$ ; more preferably  $0 < a1 \leq 0.7$ ,  $0 \leq a2 \leq 0.7$ ,  $0 \leq b1 \leq 0.5$ ,  $0 \leq b2 \leq 0.5$ ,  $0 \leq c1 \leq 0.3$ ,  $0 \leq c2 \leq 0.3$ ,  $0 \leq c3 \leq 0.3$ ,  $0 \leq c4 \leq 0.3$ ,  $0 \leq d \leq 0.3$ ,  $0 \leq e \leq 0.3$ , and  $0 \leq f \leq 0.3$ . It is noted that  $a1 + a2 + b1 + b2 + c1 + c2 + c3 + c4 + d + e + f \leq 1.0$ .

[0191] The polymer should preferably have a weight average molecular weight (M<sub>w</sub>) in the range of 1,000 to 500,000, and more preferably 3,000 to 100,000, as measured by GPC versus polystyrene standards using tetrahydrofuran (THF) or N,N-dimethylformamide (DMF) solvent. A M<sub>w</sub> in the range ensures that the resist film has etch resistance and eliminates the risk of resolution decline by a failure to provide a difference in dissolution rate before and after exposure.

[0192] The influence of M<sub>w</sub>/M<sub>n</sub> becomes stronger as the pattern rule becomes finer. Therefore, the polymer should preferably have a narrow dispersity (M<sub>w</sub>/M<sub>n</sub>) of 1.0 to 2.0 in order to provide a resist composition suitable for micropatterning to a small feature size. A M<sub>w</sub>/M<sub>n</sub> in the range ensures that the contents of lower and higher molecular weight polymer fractions are low and eliminates a possibility that foreign matter is left on the pattern or the pattern profile is degraded.

[0193] The polymer may be synthesized, for example, by dissolving a monomer or monomers corresponding to the above-mentioned repeat units in an organic solvent, adding a radical polymerization initiator, and heating for polymerization.

[0194] Examples of the organic solvent which can be used for polymerization include toluene, benzene, THF, diethyl ether, dioxane, cyclohexane, cyclopentane, methyl ethyl ketone (MEK), propylene glycol monomethyl ether acetate (PGMEA), and γ-butyrolactone (GBL). Examples of the polymerization initiator used herein include 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis(2,4-dimethylvaleronitrile), dimethyl 2,2'-azobis(2-methylpropionate), 1,1'-azobis(1-acetoxy-1-phenylethane), benzoyl peroxide, and lauroyl peroxide. The initiator is preferably added in an amount of 0.01 to 25 mol % based on the total of monomers to be polymerized. The reaction temperature is preferably 50 to 150° C., more preferably 60 to 100° C. The reaction time is preferably 2 to 24 hours, more preferably 2 to 12 hours in view of production efficiency.

[0195] The polymerization initiator may be fed to the reactor either by adding the initiator to the monomer solution and feeding the solution to the reactor, or by dissolving the initiator in a solvent

to form an initiator solution and feeding the initiator solution and the monomer solution independently to the reactor. Because of a possibility that in the standby duration, the initiator generates a radical which triggers polymerization reaction to form a ultra-high-molecular-weight polymer, it is preferred from the standpoint of quality control to prepare the monomer solution and the initiator solution separately and add them dropwise. The acid labile group that has been incorporated in the monomer may be kept as such, or polymerization may be followed by protection or partial protection. During the polymer synthesis, any known chain transfer agent such as dodecyl mercaptan or 2-mercaptoethanol may be added for molecular weight control purpose. The amount of chain transfer agent added is preferably 0.01 to 20 mol % based on the total of monomers.

[0196] When a hydroxy-containing monomer is copolymerized, the hydroxy group is substituted by an acetal group which is susceptible to deprotection with acid, typically ethoxyethoxy, prior to polymerization, and the polymerization is followed by deprotection with weak acid and water. Alternatively, the hydroxy group is substituted by an acetyl, formyl or pivaloyl group prior to polymerization, and the polymerization is followed by alkaline hydrolysis.

[0197] When hydroxystyrene or hydroxyvinyl naphthalene is copolymerized, one method is dissolving hydroxystyrene or hydroxyvinyl naphthalene and other monomers in an organic solvent, adding a radical polymerization initiator thereto, and heating the solution for polymerization. In an alternative method, acetoxystyrene or acetoxylvinyl naphthalene is used instead, and after polymerization, the acetoxyl group is deprotected by alkaline hydrolysis, for thereby converting the polymer product to polyhydroxystyrene or polyhydroxyvinyl naphthalene.

[0198] For alkaline hydrolysis, a base such as aqueous ammonia or triethylamine may be used. Preferably the reaction temperature is  $-20^{\circ}\text{C.}$  to  $100^{\circ}\text{C.}$ , more preferably  $0^{\circ}\text{C.}$  to  $60^{\circ}\text{C.}$ , and the reaction time is 0.2 to 100 hours, more preferably 0.5 to 20 hours.

[0199] The amounts of monomers in the monomer solution may be determined appropriate so as to provide the preferred fractions of repeat units.

[0200] It is now described how to use the polymer obtained by the above preparation method. The reaction solution resulting from polymerization reaction may be used as the final product.

Alternatively, the polymer may be recovered in powder form through a purifying step such as re-precipitation step of adding the polymerization solution to a poor solvent and letting the polymer precipitate as powder, after which the polymer powder is used as the final product. It is preferred from the standpoints of operation efficiency and consistent quality to handle a polymer solution which is obtained by dissolving the powder polymer resulting from the purifying step in a solvent, as the final product.

[0201] The solvents which can be used herein are described in JP-A 2008-111103, paragraphs [0144]-[0145](U.S. Pat. No. 7,537,880). Exemplary solvents include ketones such as cyclohexanone and methyl-2-n-pentyl ketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; keto-alcohols such as diacetone alcohol (DAA); ethers such as propylene glycol monomethyl ether (PGME), ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; esters such as propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, tert-butyl acetate, tert-butyl propionate, and propylene glycol mono-tert-butyl ether acetate; lactones such as  $\gamma$ -butyrolactone (GBL); and high-boiling alcohols such as diethylene glycol, propylene glycol, glycerol, 1,4-butanediol, and 1,3-butanediol, which may be used alone or in admixture.

[0202] The polymer solution preferably has a polymer concentration of 0.01 to 30% by weight, more preferably 0.1 to 20% by weight.

[0203] Prior to use, the reaction solution or polymer solution is preferably filtered through a filter. Filtration is effective for consistent quality because foreign particles and gel which can cause

defects are removed.

[0204] Suitable materials of which the filter is made include fluorocarbon, cellulose, nylon, polyester, and hydrocarbon base materials. Preferred for the filtration of a resist composition are filters made of fluorocarbons commonly known as Teflon®, hydrocarbons such as polyethylene and polypropylene, and nylon. While the pore size of the filter may be selected appropriate to comply with the desired cleanness, the filter preferably has a pore size of up to 100 nm, more preferably up to 20 nm. A single filter may be used or a plurality of filters may be used in combination. Although the filtering method may be single pass of the solution, preferably the filtering step is repeated by flowing the solution in a circulating manner. In the polymer preparation process, the filtering step may be carried out any times, in any order and in any stage. The reaction solution as polymerized or the polymer solution may be filtered, preferably both are filtered.

[0205] The base polymer (B) may be used alone or as a blend of two or more polymers which differ in compositional ratio, Mw and/or Mw/Mn. Component (B) may also be a blend of the base polymer defined above and a hydrogenated product of ROMP. For the ROMP, reference is made to JP-A 2003-066612.

#### (C) Organic Solvent

[0206] The resist composition may comprise an organic solvent as component (C). The organic solvent (C) is not particularly limited as long as the foregoing and other components are soluble therein. Suitable solvents include ketones such as cyclopentanone, cyclohexanone, and methyl-2-n-pentyl ketone; alcohols such as 3-methoxybutanol, 3-methyl-3-methoxybutanol, 1-methoxy-2-propanol, and 1-ethoxy-2-propanol; keto-alcohols such as diacetone alcohol (DAA); ethers such as propylene glycol monomethyl ether (PGME), ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol dimethyl ether, and diethylene glycol dimethyl ether; esters such as propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether acetate, ethyl lactate, ethyl pyruvate, butyl acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, tert-butyl acetate, tert-butyl propionate, and propylene glycol mono-tert-butyl ether acetate; and lactones such as  $\gamma$ -butyrolactone (GBL), and mixtures thereof.

[0207] Of the foregoing organic solvents, it is recommended to use 1-ethoxy-2-propanol, PGMEA, cyclohexanone, GBL, DAA and mixtures thereof because the base polymer (B) is most soluble therein.

[0208] The organic solvent (C) is preferably added in an amount of 200 to 5,000 parts by weight, and more preferably 400 to 3,500 parts by weight per 80 parts by weight of the base polymer (B). The organic solvent may be used alone or in admixture.

#### (D) Photoacid Generator

[0209] The chemically amplified resist composition may comprise (D) a photoacid generator. The PAG is not particularly limited as long as it is capable of generating an acid having a higher acid strength than the sulfonic acid generated by the quencher or onium salt (A), upon exposure to high-energy radiation.

[0210] The preferred PAG is a salt having the formula (2) or (3).

##STR00505##

[0211] In formula (2), R<sup>sup.101</sup> to R<sup>sup.105</sup> are each independently a C<sub>sub.1</sub>-C<sub>sub.20</sub> hydrocarbyl group which may contain a heteroatom. Any two of R<sup>sup.101</sup>, R<sup>sup.102</sup> and R<sup>sup.103</sup> may bond together to form a ring with the sulfur atom to which they are attached. Examples of the hydrocarbyl group are as exemplified above for R<sup>sup.ct1</sup> to R<sup>sup.ct5</sup> in formulae (cation-1) and (cation-2).

[0212] Examples of the sulfonium cation in the salt having formula (2) are as exemplified above for the sulfonium cation having formula (cation-1). Examples of the iodonium cation in the salt having formula (3) are as exemplified above for the iodonium cation having formula (cation-2).

[0213] In formulae (2) and (3), X<sup>sup.-</sup> is an anion of strong acid selected from formulae (c1-1) to

(c1-5).

[0214] Compounds having the formula (4) are also preferred as the PAG (D).

##STR00506##

[0215] In formula (4), R<sup>sup</sup>.201 and R<sup>sup</sup>.202 are each independently a C<sub>sub</sub>.1-C<sub>sub</sub>.30 hydrocarbyl group which may contain a heteroatom. R<sup>sup</sup>.203 is a C<sub>sub</sub>.1-C<sub>sub</sub>.30 hydrocarbylene group which may contain a heteroatom. Any two of R<sup>sup</sup>.201, R<sup>sup</sup>.202 and R<sup>sup</sup>.203 may bond together to form a ring with the sulfur atom to which they are attached.

[0216] The C<sub>sub</sub>.1-C<sub>sub</sub>.30 hydrocarbyl group represented by R<sup>sup</sup>.201 and R<sup>sup</sup>.202 may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C<sub>sub</sub>.1-C<sub>sub</sub>.30 alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, tert-pentyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, and n-decyl; C<sub>sub</sub>.3-C<sub>sub</sub>.30 cyclic saturated hydrocarbyl groups such as cyclopentyl, cyclohexyl, cyclopentylmethyl, cyclopentylethyl, cyclopentylbutyl, cyclohexylmethyl, cyclohexylethyl, cyclohexylbutyl, norbornyl, oxanorbornyl, tricyclo[5.2.1.0<sup>sup</sup>.2,6]decyl, and adamantyl; and C<sub>sub</sub>.6-C<sub>sub</sub>.30 aryl groups such as phenyl, methylphenyl, ethylphenyl, n-propylphenyl, isopropylphenyl, n-butylphenyl, isobutylphenyl, sec-butylphenyl, tert-butylphenyl, naphthyl, methylnaphthyl, ethylnaphthyl, n-propylnaphthyl, isopropylnaphthyl, n-butylnaphthyl, isobutylnaphthyl, sec-butylnaphthyl, tert-butylnaphthyl, and anthracenyl, and combinations thereof. In these hydrocarbyl groups, some or all of the hydrogen atoms may be substituted by a moiety containing a heteroatom such as oxygen, sulfur, nitrogen or halogen, and some constituent —CH<sub>sub</sub>.2— may be replaced by a moiety containing a heteroatom such as oxygen, sulfur or nitrogen, so that the group may contain a hydroxy, cyano, fluorine, chlorine, bromine, iodine, carbonyl, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring, carboxylic anhydride (—C(=O)—O—C(=O)—) or haloalkyl moiety.

[0217] The C<sub>sub</sub>.1-C<sub>sub</sub>.30 hydrocarbylene group R<sup>sup</sup>.203 may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C<sub>sub</sub>.1-C<sub>sub</sub>.30 alkanediyl groups such as methanediyl, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,3-diyl, butane-1,4-diyl, pentane-1,5-diyl, hexane-1,6-diyl, heptane-1,7-diyl, octane-1,8-diyl, nonane-1,9-diyl, decane-1,10-diyl, undecane-1,11-diyl, dodecane-1,12-diyl, tridecane-1,13-diyl, tetradecane-1,14-diyl, pentadecane-1,15-diyl, hexadecane-1,16-diyl, and heptadecane-1,17-diyl; C<sub>sub</sub>.3-C<sub>sub</sub>.30 cyclic saturated hydrocarbylene groups such as cyclopentanedyl, cyclohexanedyl, norbornanedyl and adamantanedyl; and arylene groups such as phenylene, methylphenylene, ethylphenylene, n-propylphenylene, isopropylphenylene, n-butylphenylene, isobutylphenylene, sec-butylphenylene, tert-butylphenylene, naphthylene, methylnaphthylene, ethylnaphthylene, n-propylnaphthylene, isopropylnaphthylene, n-butylnaphthylene, isobutylnaphthylene, sec-butylnaphthylene, and tert-butylnaphthylene. In these hydrocarbylene groups, some or all of the hydrogen atoms may be substituted by a moiety containing a heteroatom such as oxygen, sulfur, nitrogen or halogen, or some constituent —CH<sub>sub</sub>.2— may be replaced by a moiety containing a heteroatom such as oxygen, sulfur or nitrogen, so that the group may contain a hydroxy, cyano, fluorine, chlorine, bromine, iodine, carbonyl, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring, carboxylic anhydride (—C(=O)—O—C(=O)—) or haloalkyl moiety. Of the heteroatoms, oxygen is preferred.

[0218] In formula (4), L<sup>sup</sup>.11 is a single bond, ether bond or a C<sub>sub</sub>.1-C<sub>sub</sub>.20 hydrocarbylene group which may contain a heteroatom. The hydrocarbylene group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are as exemplified above for the hydrocarbylene group R<sup>sup</sup>.203.

[0219] In formula (4), X<sup>sup</sup>.a, X<sup>sup</sup>.b, X<sup>sup</sup>.c and X<sup>sup</sup>.d are each independently hydrogen, fluorine or trifluoromethyl, at least one of X<sup>sup</sup>.a, X<sup>sup</sup>.b, X<sup>sup</sup>.c and X<sup>sup</sup>.d being fluorine or trifluoromethyl.

[0220] Of the PAGs having formula (4), those having formula (4') are preferred.

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[0221] In formula (4'), L.sup.11 is as defined above. X.sup.e is hydrogen or trifluoromethyl, preferably trifluoromethyl. R.sup.301, R.sup.302 and R.sup.303 are each independently hydrogen or a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom. The hydrocarbyl group may be saturated or unsaturated and straight, branched or cyclic. Examples thereof are as exemplified above for R.sup.fa1 in formula (c1-1-1). The subscripts p and q are each independently an integer of 0 to 5, and r is an integer of 0 to 4.

[0222] Examples of the PAG having formula (4) include those exemplified for the PAG having formula (2) in JP-A 2017-026980.

[0223] Of the foregoing PAGs, those having an anion of formula (c1-1-1) or (c1-4) are especially preferred because of reduced acid diffusion and high solubility in solvents. Also those having formula (4') are especially preferred because of extremely reduced acid diffusion.

[0224] When used, the PAG (D) is preferably added in an amount of 0.1 to 40 parts, and more preferably 0.5 to 20 parts by weight per 80 parts by weight of the base polymer (B). As long as the amount of the PAG is in the range, good resolution is achievable and the risk of foreign particles being formed after development or during stripping of resist film is avoided. The PAG may be used alone or in admixture.

(E) Other Quencher

[0225] The resist composition may further comprise (E) a quencher other than component (A).

[0226] Onium salts having the formula (5) are useful as the other quencher (E).

R.sup.401—CO.sub.2.sup.—Mq.sup.+ (5)

[0227] In formula (5), R.sup.401 is hydrogen or a C.sub.1-C.sub.40 hydrocarbyl group which may contain a heteroatom.

[0228] The C.sub.1-C.sub.40 hydrocarbyl group R.sup.401 may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include C.sub.1-C.sub.40 alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, tert-pentyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, and n-decyl; C.sub.3-C.sub.40 cyclic saturated hydrocarbyl groups such as cyclopentyl, cyclohexyl, cyclopentylmethyl, cyclopentylethyl, cyclopentylbutyl, cyclohexylmethyl, cyclohexylethyl, cyclohexylbutyl, norbornyl, tricyclo[5.2.1.0.sup.2,6]decyl, and adamantyl; C.sub.6-C.sub.40 aryl groups such as phenyl, naphthyl and anthracenyl, and combinations thereof. In these hydrocarbyl groups, some or all hydrogen atoms may be substituted by a moiety containing a heteroatom such as oxygen, sulfur, nitrogen or halogen, or some constituent —CH.sub.2— may be replaced by a moiety containing a heteroatom such as oxygen, sulfur or nitrogen, so that the group may contain a hydroxy, fluorine, chlorine, bromine, iodine, cyano, carbonyl, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring, carboxylic anhydride (—C(=O)—O—C(=O)—) or haloalkyl moiety. Also included are fluorinated saturated hydrocarbyl groups such as trifluoromethyl and trifluoroethyl and fluorinated aryl groups such as pentafluorophenyl and 4-trifluoromethylphenyl.

[0229] Examples of the anion in the onium salt having formula (5) are shown below, but not limited thereto.

##STR00508## ##STR00509## ##STR00510## ##STR00511## ##STR00512##

[0230] In formula (5), Mq.sup.+ is an onium cation, which is preferably selected from sulfonium cations having formula (cation-1), iodonium cations having formula (cation-2), and ammonium cations having formula (cation-3).

[0231] Examples of the onium salt having formula (5) include arbitrary combinations of anions with cations, both as exemplified above. These onium salts may be readily prepared by ion exchange reaction using any well-known organic chemistry technique. For the ion exchange reaction, reference may be made to JP-A 2007-145797, for example.

[0232] The onium salt having formula (5) functions as a quencher in the chemically amplified

resist composition because the counter anion of the onium salt is a conjugated base of a weak acid. As used herein, the weak acid indicates an acidity insufficient to deprotect an acid labile group from an acid labile group-containing unit in the base polymer. The onium salt having formula (5) functions as a quencher when used in combination with an onium salt type PAG having a conjugated base of a strong acid (typically sulfonic acid) as the counter anion. In a system using a mixture of an onium salt capable of generating a strong acid (typically sulfonic acid) and an onium salt capable of generating a weak acid (typically carboxylic acid), if the strong acid generated from the PAG upon exposure to high-energy radiation collides with the unreacted onium salt having a weak acid anion, then a salt exchange occurs whereby the weak acid is released and an onium salt having a strong acid anion is formed. In this course, the strong acid is exchanged into the weak acid having a low catalysis, incurring apparent deactivation of the acid for enabling to control acid diffusion.

[0233] Also useful as the other quencher (E) are onium salts having sulfonium cation and phenoxide anion sites in a common molecule as described in JP 6848776, onium salts having sulfonium cation and carboxylate anion sites in a common molecule as described in JP 6583136 and JP-A 2020-200311, and onium salts having iodonium cation and carboxylate anion sites in a common molecule as described in JP 6274755.

[0234] If a PAG capable of generating a strong acid is an onium salt, an exchange from the strong acid generated upon exposure to high-energy radiation to a weak acid can take place as mentioned above, but it rarely happens that the weak acid generated upon exposure to high-energy radiation collides with the unreacted onium salt capable of generating a strong acid to induce a salt exchange. This is because of the phenomenon that an onium cation is more likely to form an ion pair with a stronger acid anion.

[0235] When the onium salt having formula (5) is used as the quencher (E), the amount of the onium salt used is preferably 0.1 to 20 parts by weight, more preferably 0.1 to 10 parts by weight per 80 parts by weight of the base polymer (B). As long as the amount of onium salt type quencher (E) is in the range, a satisfactory resolution is available without a substantial lowering of sensitivity. The onium salt having formula (5) may be used alone or in admixture.

[0236] Nitrogen-containing compounds may also be used as the other quencher (E). Suitable nitrogen-containing compounds include primary, secondary and tertiary amine compounds, specifically amine compounds having a hydroxy group, ether bond, ester bond, lactone ring, cyano group or sulfonate ester bond, as described in JP-A 2008-111103, paragraphs [0146]-[0164](U.S. Pat. No. 7,537,880), and primary or secondary amine compounds protected with a carbamate group, as described in JP 3790649.

[0237] A sulfonic acid sulfonium salt having a nitrogen-containing substituent may also be used as the nitrogen-containing compound. This compound functions as a quencher in the unexposed region, but as a so-called photo-degradable base in the exposed region because it loses the quencher function in the exposed region due to neutralization thereof with the acid generated by itself. Using a photo-degradable base, the contrast between exposed and unexposed regions can be further enhanced. With respect to the photo-degradable base, reference may be made to JP-A 2009-109595 and JP-A 2012-046501, for example.

[0238] When the nitrogen-containing compound is used as the other quencher (E), the amount of the nitrogen-containing compound used is preferably 0.001 to 12 parts by weight, more preferably 0.01 to 8 parts by weight per 80 parts by weight of the base polymer (B). The nitrogen-containing compound may be used alone or in admixture.

#### (F) Surfactant

[0239] The resist composition may further include (F) a surfactant. Preferred are a surfactant which is insoluble or substantially insoluble in water and soluble in alkaline developer, and a surfactant which is insoluble or substantially insoluble in water and alkaline developer. For the surfactant, reference should be made to those compounds described in JP-A 2010-215608 and JP-A 2011-

016746.

[0240] While many examples of the surfactant which is insoluble or substantially insoluble in water and alkaline developer are described in the patent documents cited herein, preferred examples are surfactants FC-4430 (3M), Olfine® E1004 (Nissin Chemical Co., Ltd.), Surflon® 5-381, KH-20 and KH-30 (AGC Seimi Chemical Co., Ltd.). Partially fluorinated oxetane ring-opened polymers having the formula (surf-1) are also useful.

##STR00513##

[0241] It is provided herein that R, R<sub>f</sub>, A, B, C, m, and n are applied to only formula (surf-1), independent of their descriptions other than for the surfactant. R is a di- to tetra-valent C<sub>sub</sub>.2-C<sub>sub</sub>.5 aliphatic group. Exemplary divalent aliphatic groups include ethylene, 1,4-butylene, 1,2-propylene, 2,2-dimethyl-1,3-propylene and 1,5-pentylene. Exemplary tri- and tetra-valent groups are shown below.

##STR00514##

[0242] Herein the broken line denotes a valence bond. These formulae are partial structures derived from glycerol, trimethylol ethane, trimethylol propane, and pentaerythritol, respectively. Of these, 1,4-butylene and 2,2-dimethyl-1,3-propylene are preferably used.

[0243] R<sub>f</sub> is trifluoromethyl or pentafluoroethyl, and preferably trifluoromethyl. The letter m is an integer of 0 to 3, n is an integer of 1 to 4, and the sum of m and n, which represents the valence of R, is an integer of 2 to 4. "A" is equal to 1, B is an integer of 2 to 25, and C is an integer of 0 to 10. Preferably, B is an integer of 4 to 20, and C is 0 or 1. Note that the formula (surf-1) does not prescribe the arrangement of respective constituent units while they may be arranged either blockwise or randomly. For the preparation of surfactants in the form of partially fluorinated oxetane ring-opened polymers, reference should be made to U.S. Pat. No. 5,650,483, for example.

[0244] The surfactant which is insoluble or substantially insoluble in water and soluble in alkaline developer is useful when ArF immersion lithography is applied to the resist composition in the absence of a resist protective film. In this embodiment, the surfactant has a propensity to segregate on the resist surface for achieving a function of minimizing water penetration or leaching. The surfactant is also effective for preventing water-soluble components from being leached out of the resist film for minimizing any damage to the exposure tool. The surfactant becomes solubilized during aqueous alkaline development following exposure and PEB, and thus forms few or no foreign particles which become defects. The preferred surfactant is a polymeric surfactant which is insoluble or substantially insoluble in water, but soluble in alkaline developer, also referred to as "hydrophobic resin" in this sense, and especially which is water repellent and enhances water sliding.

[0245] Suitable polymeric surfactants include those containing repeat units of at least one type selected from the formulae (6A) to (6E).

##STR00515##

[0246] Herein, R<sup>sup</sup>.B is hydrogen, fluorine, methyl or trifluoromethyl. W<sup>sup</sup>.1 is —CH<sub>sub</sub>.2—, —CH<sub>sub</sub>.2CH<sub>sub</sub>.2—, —O—, or two separate —H. R<sup>sup</sup>.s1 is each independently hydrogen or a C<sub>sub</sub>.1-C<sub>sub</sub>.10 hydrocarbyl group. R<sup>sup</sup>.s2 is a single bond or a C<sub>sub</sub>.1-C<sub>sub</sub>.5 straight or branched hydrocarbylene group. R<sup>sup</sup>.s3 is each independently hydrogen, a C<sub>sub</sub>.1-C<sub>sub</sub>.15 hydrocarbyl or fluorinated hydrocarbyl group, or an acid labile group. When R<sup>sup</sup>.s3 is a hydrocarbyl or fluorinated hydrocarbyl group, an ether bond or carbonyl moiety may intervene in a carbon-carbon bond. R<sup>sup</sup>.s4 is a C<sub>sub</sub>.1-C<sub>sub</sub>.20 (u+1)-valent hydrocarbon or fluorinated hydrocarbon group, and u is an integer of 1 to 3. R<sup>sup</sup>.s5 is each independently hydrogen or a group: —C(=O)—O—R<sup>sup</sup>.sa wherein R<sup>sup</sup>.sa is a C<sub>sub</sub>.1-C<sub>sub</sub>.20 fluorinated hydrocarbyl group. R<sup>sup</sup>.s6 is a C<sub>sub</sub>.1-C<sub>sub</sub>.15 hydrocarbyl or fluorinated hydrocarbyl group in which an ether bond or carbonyl moiety may intervene in a carbon-carbon bond.

[0247] The hydrocarbyl group represented by R<sup>sup</sup>.s1 may be straight, branched or cyclic and is preferably saturated. Examples thereof include C<sub>sub</sub>.1-C<sub>sub</sub>.10 alkyl groups such as methyl,



ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, and C.sub.3-C.sub.10 cyclic saturated hydrocarbyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, adamantyl, and norbornyl. Inter alia, C.sub.1-C.sub.6 hydrocarbyl groups are preferred.

[0248] The hydrocarbylene group represented by R.sup.s2 may be straight, branched or cyclic and is preferably saturated. Examples thereof include methylene, ethylene, propylene, butylene and pentylenes.

[0249] The hydrocarbyl group represented by R.sup.s3 or R.sup.s6 may be saturated or unsaturated and straight, branched or cyclic. Examples thereof include saturated hydrocarbyl groups, and aliphatic unsaturated hydrocarbyl groups such as alkenyl and alkynyl groups, with the saturated hydrocarbyl groups being preferred. Suitable saturated hydrocarbyl groups include those exemplified for the hydrocarbyl group represented by R.sup.s1 as well as undecyl, dodecyl, tridecyl, tetradecyl, and pentadecyl. Examples of the fluorinated hydrocarbyl group represented by R.sup.s3 or R.sup.s6 include the foregoing hydrocarbyl groups in which some or all carbon-bonded hydrogen atoms are substituted by fluorine atoms. In these groups, an ether bond or carbonyl moiety may intervene in a carbon-carbon bond as mentioned above.

[0250] Examples of the acid labile group represented by R.sup.s3 include groups of the above formulae (AL-3) to (AL-5), trialkylsilyl groups in which each alkyl moiety has 1 to 6 carbon atoms, and C.sub.4-C.sub.20 oxoalkyl groups.

[0251] The (u+1)-valent hydrocarbon or fluorinated hydrocarbon group represented by R.sup.s4 may be straight, branched or cyclic and examples thereof include the foregoing hydrocarbyl or fluorinated hydrocarbyl groups from which "u" number of hydrogen atoms are eliminated.

[0252] The fluorinated hydrocarbyl group represented by R.sup.sa may be straight, branched or cyclic and is preferably saturated. Examples thereof include the foregoing hydrocarbyl groups in which some or all hydrogen atoms are substituted by fluorine atoms. Illustrative examples include trifluoromethyl, 2,2,2-trifluoroethyl, 3,3,3-trifluoro-1-propyl, 3,3,3-trifluoro-2-propyl, 2,2,3,3-tetrafluoropropyl, 1,1,1,3,3,3-hexafluoroisopropyl, 2,2,3,3,4,4,4-heptafluorobutyl, 2,2,3,3,4,4,5,5-octafluoropentyl, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl, 2-(perfluorobutyl)ethyl, 2-(perfluorohexyl)ethyl, 2-(perfluorooctyl)ethyl, and 2-(perfluorodecyl)ethyl.

[0253] Examples of the repeat units having formulae (6A) to (6E) are shown below, but not limited thereto. Herein R.sup.B is as defined above.

##STR00516## ##STR00517## ##STR00518## ##STR00519## ##STR00520## ##STR00521## ##STR00522## ##STR00523##

[0254] The polymeric surfactant may further contain repeat units other than the repeat units having formulae (6A) to (6E). Typical other repeat units are those derived from methacrylic acid and  $\alpha$ -trifluoromethylacrylic acid derivatives. In the polymeric surfactant, the content of the repeat units having formulae (6A) to (6E) is preferably at least 20 mol %, more preferably at least 60 mol %, most preferably 100 mol % of the overall repeat units.

[0255] The polymeric surfactant preferably has a Mw of 1,000 to 500,000, more preferably 3,000 to 100,000 and a Mw/Mn of 1.0 to 2.0, more preferably 1.0 to 1.6.

[0256] The polymeric surfactant may be synthesized by any desired method, for example, by dissolving an unsaturated bond-containing monomer or monomers providing repeat units having formula (6A) to (6E) and optionally other repeat units in an organic solvent, adding a radical initiator, and heating for polymerization. Suitable organic solvents used herein include toluene, benzene, THF, diethyl ether, and dioxane. Examples of the polymerization initiator used herein include AIBN, 2,2'-azobis(2,4-dimethylvaleronitrile), dimethyl 2,2-azobis(2-methylpropionate), benzoyl peroxide, and lauroyl peroxide. Preferably the reaction temperature is 50 to 100° C. and the reaction time is 4 to 24 hours. The acid labile group that has been incorporated in the monomer may be kept as such, or the polymer may be protected or partially protected therewith at the end of polymerization.

[0257] During the synthesis of polymeric surfactant, any known chain transfer agent such as dodecyl mercaptan or 2-mercaptoethanol may be added for molecular weight control purpose. The amount of chain transfer agent added is preferably 0.01 to 10 mol % based on the total moles of monomers to be polymerized.

[0258] When the resist composition contains a surfactant (F), the amount thereof is preferably 0.1 to 50 parts by weight, and more preferably 0.5 to 10 parts by weight per 80 parts by weight of the base polymer (B). At least 0.1 part of the surfactant is effective in improving the receding contact angle with water of the resist film at its surface. Up to 50 parts of the surfactant is effective in forming a resist film having a low rate of dissolution in a developer and capable of maintaining the height of a small-size pattern formed therein. The surfactant (F) may be used alone or in admixture.

#### (G) Other Components

[0259] The resist composition may further comprise (G) another component, for example, a compound which is decomposed with an acid to generate another acid (i.e., acid amplifier compound), an organic acid derivative, a fluorinated alcohol, and a compound having a Mw of up to 3,000 which changes its solubility in developer under the action of an acid (i.e., dissolution inhibitor). Specifically, the acid amplifier compound is described in JP-A 2009-269953 and JP-A 2010-215608 and preferably used in an amount of 0 to 5 parts, more preferably 0 to 3 parts by weight per 80 parts by weight of the base polymer (B). An extra amount of the acid amplifier compound can make the acid diffusion control difficult and cause degradations to resolution and pattern profile. With respect to the remaining additives, reference should be made to JP-A 2009-269953 and JP-A 2010-215608.

#### [Process]

[0260] A further embodiment of the invention is a process of forming a pattern from the resist composition defined above by lithography. The preferred process includes the steps of applying the resist composition onto a substrate to form a resist film thereon, exposing the resist film to high-energy radiation, and developing the exposed resist film in a developer. Any desired steps may be added to the process if necessary.

[0261] The substrate used herein may be a substrate for integrated circuitry fabrication, e.g., Si, SiO<sub>2</sub>, SiN, SiON, TiN, WSi, BPSG, SOG, organic antireflective film, etc. or a substrate for mask circuitry fabrication, e.g., Cr, CrO, CrON, MoSi<sub>2</sub>, SiO<sub>2</sub>, etc.

[0262] The resist composition is applied onto a substrate by a suitable coating technique such as spin coating. The coating is prebaked on a hot plate preferably at a temperature of 60 to 150° C. for 1 to 10 minutes, more preferably at 80 to 140° C. for 1 to 5 minutes. The resulting resist film preferably has a thickness of 0.05 to 2 μm.

[0263] Then the resist film is exposed to a pattern of high-energy radiation, typically KrF or ArF excimer laser, EUV or EB. On use of KrF excimer laser, ArF excimer laser or EUV, the resist film is exposed through a mask having a desired pattern, preferably in a dose of 1 to 200 mJ/cm<sup>2</sup>, more preferably 10 to 100 mJ/cm<sup>2</sup>. On use of EB, a pattern may be written directly or through a mask having the desired pattern, preferably in a dose of 1 to 300 μC/cm<sup>2</sup>, more preferably 10 to 200 μC/cm<sup>2</sup>.

[0264] The exposure may be performed by conventional lithography whereas the immersion lithography of holding a liquid having a refractive index of at least 1.0 between the resist film and the projection lens may be employed if desired. The liquid is typically water, and in this case, a protective film which is insoluble in water may be formed on the resist film.

[0265] While the water-insoluble protective film serves to prevent any components from being leached out of the resist film and to improve water sliding on the film surface, it is generally divided into two types. The first type is an organic solvent-strippable protective film which must be stripped, prior to alkaline development, with an organic solvent in which the resist film is not dissolvable. The second type is an alkali-soluble protective film which is soluble in an alkaline developer so that it can be removed simultaneously with the removal of solubilized regions of the

resist film. The protective film of the second type is preferably of a material comprising a polymer having a 1,1,1,3,3,3-hexafluoro-2-propanol residue (which is insoluble in water and soluble in an alkaline developer) as a base in an alcohol solvent of at least 4 carbon atoms, an ether solvent of 8 to 12 carbon atoms or a mixture thereof. Alternatively, the aforementioned surfactant which is insoluble in water and soluble in an alkaline developer may be dissolved in an alcohol solvent of at least 4 carbon atoms, an ether solvent of 8 to 12 carbon atoms or a mixture thereof to form a material from which the protective film of the second type is formed.

[0266] After the exposure, the resist film may be baked (PEB), for example, on a hotplate preferably at 60 to 150° C. for 1 to 5 minutes, more preferably at 80 to 140° C. for 1 to 3 minutes.

[0267] The resist film is then developed with a developer in the form of an aqueous base solution, for example, 0.1 to 5 wt %, preferably 2 to 3 wt % aqueous solution of tetramethylammonium hydroxide (TMAH) for 0.1 to 3 minutes, preferably 0.5 to 2 minutes by conventional techniques such as dip, puddle and spray techniques. In this way, the exposed region of the resist film is dissolved away, and a desired resist pattern is formed on the substrate.

[0268] Any desired step may be added to the pattern forming process. For example, after the resist film is formed, a step of rinsing with pure water may be introduced to extract the acid generator or the like from the film surface or wash away particles. After exposure, a step of rinsing may be introduced to remove any water remaining on the film after exposure.

[0269] Also, a double patterning process may be used for pattern formation. The double patterning process includes a trench process of processing an underlay to a 1:3 trench pattern by a first step of exposure and etching, shifting the position, and forming a 1:3 trench pattern by a second step of exposure, for forming a 1:1 pattern; and a line process of processing a first underlay to a 1:3 isolated left pattern by a first step of exposure and etching, shifting the position, processing a second underlay formed below the first underlay by a second step of exposure through the 1:3 isolated left pattern, for forming a half-pitch 1:1 pattern.

[0270] In the pattern forming process, negative tone development may also be used. That is, an organic solvent may be used instead of the aqueous alkaline solution as the developer for developing and dissolving away the unexposed region of the resist film.

[0271] The organic solvent used as the developer is preferably selected from 2-octanone, 2-nonanone, 2-heptanone, 3-heptanone, 4-heptanone, 2-hexanone, 3-hexanone, diisobutyl ketone, methylcyclohexanone, acetophenone, methylacetophenone, propyl acetate, butyl acetate, isobutyl acetate, pentyl acetate, isopentyl acetate, butenyl acetate, propyl formate, butyl formate, isobutyl formate, pentyl formate, isopentyl formate, methyl valerate, methyl pentenoate, methyl crotonate, ethyl crotonate, methyl propionate, ethyl propionate, ethyl 3-ethoxypropionate, methyl lactate, ethyl lactate, propyl lactate, butyl lactate, isobutyl lactate, pentyl lactate, isopentyl lactate, methyl 2-hydroxyisobutyrate, ethyl 2-hydroxyisobutyrate, methyl benzoate, ethyl benzoate, phenyl acetate, benzyl acetate, methyl phenylacetate, ethyl phenylacetate, benzyl formate, phenylethyl formate, methyl 3-phenylpropionate, benzyl propionate, and 2-phenylethyl acetate. These organic solvents may be used alone or in admixture of two or more.

## EXAMPLES

[0272] Synthesis Examples, Examples and Comparative Examples are given below by way of illustration and not by way of limitation. The abbreviation “pbw” is parts by weight. Analysis is made by time-of-flight mass spectrometry using the instrument, MALDI TOF-MS: S3000 by JEOL Ltd.

### [1] Synthesis of Onium Salts

#### [Example 1-1] Synthesis of Onium Salt PDQ-1

##STR00524##

#### (1) Synthesis of Intermediate In-1

[0273] In a reactor under nitrogen atmosphere, 50.0 g of Reactant SM-1, 27.4 g of potassium carbonate, and 2.7 g of sodium iodide were dissolved in 300 g of DMF. The reactor was heated at

an internal temperature of 45° C., whereupon 23.9 g of Reactant SM-2 was added dropwise. At the end of addition, the solution was heated at a temperature of 65° C. and aged for 18 hours. The aged reaction solution was cooled in an ice bath, after which 300 g of water was added dropwise to quench the reaction. The end compound was extracted with 250 mL of ethyl acetate and 150 mL of toluene, followed by ordinary aqueous work-up and solvent distillation. There was obtained Intermediate In-1 as oily matter (amount 61.6 g, yield 95%).

## (2) Synthesis of Onium Salt PDQ-1

[0274] In a reactor under nitrogen atmosphere, 10.9 g of Intermediate In-1 was dissolved in 50 g of THF. The reactor was heated at an internal temperature of 45° C., whereupon 6.2 g of 25 wt % sodium hydroxide aqueous solution was added dropwise. After the addition, the solution was aged at the temperature of 45° C. for 13 hours. Once the disappearance of Intermediate In-1 was confirmed by thin-layer chromatography, the reaction solution was cooled to room temperature. After cooling, 14.3 g of Reactant SM-3, 100 g of methyl isobutyl ketone, and 50 g of water were added to the solution, which was stirred at room temperature for 30 minutes. At the end of stirring, the organic layer was taken out, washed with water, and concentrated under reduced pressure. The concentrate was purified by silica gel chromatography, obtaining the target Onium Salt PDQ-1 as oily matter (amount 16.7 g, yield 84%).

[0275] PDQ-1 was analyzed by TOF-MS, with the data shown below.

[0276] MALDI TOF-MS: [0277] positive M.sup.+ 317 (corresponding to C.sub.18H.sub.12F.sub.3S.sup.+) [0278] negative M.sup.- 347 (corresponding to C.sub.12H.sub.12IO.sub.4.sup.-)

## [Examples 1-2 to 1-7] Synthesis of Onium Salts PDQ-2 to PDQ-7

[0279] Onium salts PDQ-2 to PDQ-7 shown below were synthesized using corresponding reactants and well-known organic synthesis reactions.

##STR00525## ##STR00526##

## [2] Synthesis of Base Polymers

### [Synthesis Example] Synthesis of Base Polymers P-1 to P-5

[0280] Base polymers P-1 to P-5 were synthesized by combining monomers, performing copolymerization reaction in MEK solvent, pouring the reaction solution to hexane for precipitation, washing the solid precipitate with hexane, isolation and drying. The polymer was analyzed for composition by <sup>1</sup>H-NMR spectroscopy and for Mw and Mw/Mn by GPC versus polystyrene standards using DMF solvent.

##STR00527## ##STR00528## ##STR00529##

## [3] Preparation of Chemically Amplified Resist Compositions

### Examples 2-1 to 2-30 and Comparative Examples 1-1 to 1-20

[0281] Chemically amplified resist compositions (R-1 to R-30, CR-1 to CR-20) in solution form were prepared by dissolving a quencher (PDQ-1 to PDQ-7) or comparative quencher (PDQ-A to PDQ-D), photoacid generator (PAG-X and PAG-Y), base polymer (P-1 to P-5), and other quencher (AQ-1 and AQ-2) in a solvent containing 0.01 wt % of surfactant A in accordance with the formulation shown in Tables 1 and 2, and filtering through a Teflon® filter with a pore size of 0.2 μm.

TABLE-US-00001  
TABLE 1 Base Photoacid Other Resist polymer Quencher generator quencher  
Solvent 1 Solvent 2 composition (pbw) (pbw) (pbw) (pbw) (pbw) (pbw) Example 2-1 R-1 P-1 (80) PDQ-1 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-2 R-2 P-1 (80) PDQ-2 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-3 R-3 P-1 (80) PDQ-3 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-4 R-4 P-1 (80) PDQ-4 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-5 R-5 P-1 (80) PDQ-5 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-6 R-6 P-1 (80) PDQ-6 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-7 R-7 P-1 (80) PDQ-7 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-8 R-8 P-1 (80) PDQ-1 (5) PAG-Y (15) — PGMEA (2200) DAA (900) 2-9 R-9 P-1 (80) PDQ-1 (2.5) PAG-X (15) AQ-1 (2.5) PGMEA (2200) DAA (900) 2-10 R-10 P-1 (80) PDQ-2 (3)

PAG-Y (15) AQ-2 (2) PGMEA (2200) DAA (900) 2-11 R-11 P-2 (80) PDQ-1 (5) PAG-X (14) — PGMEA (2200) DAA (900) 2-12 R-12 P-2 (80) PDQ-2 (5) PAG-X (15) — PGMEA (2200) DAA (900) 2-13 R-13 P-2 (80) PDQ-4 (5) PAG-Y (14) — PGMEA (2200) DAA (900) 2-14 R-14 P-2 (80) PDQ-6 (5) PAG-Y (15) — PGMEA (2200) DAA (900) 2-15 R-15 P-2 (80) PDQ-1 (4) PAG-X (15) AQ-1 (2) PGMEA (2200) DAA (900) 2-16 R-16 P-3 (80) PDQ-1 (5) — — PGMEA (2200) DAA (900) 2-17 R-17 P-3 (80) PDQ-2 (5) — — PGMEA (2200) DAA (900) 2-18 R-18 P-3 (80) PDQ-3 (5) — — PGMEA (2200) DAA (900) 2-19 R-19 P-3 (80) PDQ-4 (5) PAG-X (5) — PGMEA (2200) DAA (900) 2-20 R-20 P-3 (80) PDQ-2 (3) — AQ-1 (2) PGMEA (2200) DAA (900) 2-21 R-21 P-4 (80) PDQ-1 (5) — — PGMEA (2200) DAA (900) 2-22 R-22 P-4 (80) PDQ-2 (5) — — PGMEA (2200) DAA (900) 2-23 R-23 P-4 (80) PDQ-5 (5) — — PGMEA (2200) DAA (900) 2-24 R-24 P-4 (80) PDQ-6 (6) PAG-Y (5) — PGMEA (2200) DAA (900) 2-25 R-25 P-4 (80) PDQ-2 (5) — — PGMEA (2200) DAA (900) 2-26 R-26 P-5 (80) PDQ-1 (5) — — PGMEA (2200) DAA (900) 2-27 R-27 P-5 (80) PDQ-2 (5) — — PGMEA (2200) DAA (900) 2-28 R-28 P-5 (80) PDQ-7 (3) PAG-Y (5) AQ-2 (2) PGMEA (2200) DAA (900) 2-29 R-29 P-5 (80) PDQ-3 (5) — — PGMEA (2200) DAA (900) 2-30 R-30 P-5 (80) PDQ-2 (2.5) — AQ-1 (2.5) PGMEA (2200) DAA (900)

TABLE-US-00002 TABLE 2 Base Comparative Photoacid Other Resist polymer Quencher generator quencher Solvent 1 Solvent 2 composition (pbw) (pbw) (pbw) (pbw) (pbw) (pbw) Comparative 1-1 CR-1 P-1 (80) PDQ-A (5) PAG-X (15) — PGMEA (2200) DAA (900) Example 1-2 CR-2 P-1 (80) PDQ-B (5) PAG-X (15) — PGMEA (2200) DAA (900) 1-3 CR-3 P-1 (80) PDQ-C (5) PAG-X (15) — PGMEA (2200) DAA (900) 1-4 CR-4 P-1 (80) PDQ-D (5) PAG-X (15) — PGMEA (2200) DAA (900) 1-5 CR-5 P-1 (80) PDQ-A (5) PAG-Y (15) — PGMEA (2200) DAA (900) 1-6 CR-6 P-1 (80) PDQ-B (5) PAG-Y (15) — PGMEA (2200) DAA (900) 1-7 CR-7 P-1 (80) PDQ-C (2.5) PAG-X (15) AQ-1 (2.5) PGMEA (2200) DAA (900) 1-8 CR-8 P-1 (80) PDQ-D (3) PAG-Y (15) AQ-2 (2) PGMEA (2200) DAA (900) 1-9 CR-9 P-2 (80) PDQ-A (5) PAG-X (15) — PGMEA (2200) DAA (900) 1-10 CR-10 P-2 (80) PDQ-B (5) PAG-X (15) — PGMEA (2200) DAA (900) 1-11 CR-11 P-2 (80) PDQ-C (4) PAG-X (15) AQ-1 (2) PGMEA (2200) DAA (900) 1-12 CR-12 P-3 (80) PDQ-A (5) — — PGMEA (2200) DAA (900) 1-13 CR-13 P-3 (80) PDQ-C (5) — — PGMEA (2200) DAA (900) 1-14 CR-14 P-3 (80) PDQ-D (3) — AQ-1 (2) PGMEA (2200) DAA (900) 1-15 CR-15 P-4 (80) PDQ-A (5) — — PGMEA (2200) DAA (900) 1-16 CR-16 P-4 (80) PDQ-D (5) — — PGMEA (2200) DAA (900) 1-17 CR-17 P-4 (80) PDQ-C (6) PAG-Y (5) — PGMEA (2200) DAA (900) 1-18 CR-18 P-5 (80) PDQ-A (5) — — PGMEA (2200) DAA (900) 1-19 CR-19 P-5 (80) PDQ-B (3) PAG-Y (5) AQ-2 (2) PGMEA (2200) DAA (900) 1-20 CR-20 P-5 (80) PDQ-C (5) — — PGMEA (2200) DAA (900)

[0282] The solvents, photoacid generators PAG-X and PAG-Y, comparative quenchers PDQ-A to PDQ-D, other quenchers AQ-1 and AQ-2, and surfactant A in Tables 1 and 2 are identified below.

[0283] Solvent: [0284] PGMEA (propylene glycol monomethyl ether acetate) [0285] DAA (diacetone alcohol)

[0286] Photoacid generators: PAG-X and PAG-Y

##STR00530##

[0287] Comparative quenchers: PDQ-A to PDQ-D

##STR00531##

[0288] Other quenchers: AQ-1 and AQ-2

##STR00532##

[0289] Surfactant A: 3-methyl-3-(2,2,2-trifluoroethoxymethyl)oxetane/tetrahydrofuran/2,2-dimethyl-1,3-propane diol copolymer (Omnova Solutions, Inc.)

##STR00533## [0290] a: (b+b'): (c+c')=1: 4-7:0.01-1 (molar ratio) [0291] Mw=1,500

[4] EUV Lithography Test 1

Examples 3-1 to 3-30 and Comparative Examples 2-1 to 2-20

[0292] Each of the chemically amplified resist compositions (R-1 to R-30, CR-1 to CR-20) was

spin coated on a silicon substrate having a 20-nm coating of silicon-containing spin-on hard mask SHB-A940 (Shin-Etsu Chemical Co., Ltd., silicon content 43 wt %) and prebaked on a hotplate at 100° C. for 60 seconds to form a resist film of 50 nm thick. Using an EUV scanner NXE3400 (ASML, NA 0.33,  $\sigma$  0.9/0.6, dipole illumination), the resist film was exposed to EUV through a mask bearing a LS pattern having a size of 18 nm and a pitch of 36 nm (on-wafer size) while varying the dose and focus (dose pitch: 1 mJ/cm.sup.2, focus pitch: 0.020  $\mu$ m). The resist film was baked (PEB) on a hotplate at the temperature shown in Tables 3 and 4 for 60 seconds and puddle developed in a 2.38 wt % TMAH aqueous solution for 30 seconds, rinsed with a rinse fluid containing surfactant, and spin dried to form a positive pattern.

[0293] The LS pattern as developed was observed under CD-SEM (CG6300, Hitachi High-Technologies Corp.) whereupon sensitivity, EL, LWR, DOF and collapse limit were evaluated by the following methods. The results are shown in Tables 3 and 4.

[Evaluation of Sensitivity]

[0294] The optimum dose Eop (mJ/cm.sup.2) which provided a LS pattern with a line width of 18 nm and a pitch of 36 nm was determined as an index of sensitivity. A smaller value indicates a higher sensitivity.

[Evaluation of EL]

[0295] The exposure dose which provided a LS pattern with a space width of 18 nm $\pm$ 10% (i.e., 16.2 to 19.8 nm) was determined. EL (%) is calculated from the exposure doses according to the following equation:

$$EL (\%) = (|E_{\text{sub.1}} - E_{\text{sub.2}}| / E_{\text{op}}) \times 100$$

[0296] wherein E.sub.1 is an optimum exposure dose which provides a LS pattern with a line width of 16.2 nm and a pitch of 36 nm, E.sub.2 is an optimum exposure dose which provides a LS pattern with a line width of 19.8 nm and a pitch of 36 nm, and Eop is an optimum exposure dose which provides a LS pattern with a line width of 18 nm and a pitch of 36 nm. A greater value indicates better performance.

[Evaluation of LWR]

[0297] For the LS pattern formed by exposure at the optimum dose Eop, the line width was measured at 10 longitudinally spaced apart points, from which a 3-fold value (3 $\sigma$ ) of the standard deviation ( $\sigma$ ) was determined and reported as LWR. A smaller value of 3 $\sigma$  indicates a pattern having small roughness and uniform line width.

[Evaluation of DOF]

[0298] As an index of DOF, a range of focus which provided a LS pattern with a size of 18 nm $\pm$ 10% (i.e., 16.2 to 19.8 nm) was determined. A greater value indicates a wider DOF.

[Evaluation of Collapse Limit of Line Pattern]

[0299] For the LS pattern formed by exposure at the dose corresponding to the optimum focus, the line width was measured at 10 longitudinally spaced apart points. The minimum line size above which lines could be resolved without collapse was determined and reported as collapse limit. A smaller value indicates better collapse limit.

TABLE-US-00003 TABLE 3 Resist PEB temp. Eop EL LWR DOF Collapse limit composition (° C.) (mJ/cm.sup.2) (%) (nm) (nm) (nm) Example 3-1 R-1 100 35 18 2.6 120 11.2 3-2 R-2 100 34 17 2.5 110 11.2 3-3 R-3 100 35 17 2.6 110 10.9 3-4 R-4 95 36 17 2.7 110 11.3 3-5 R-5 100 35 18 2.8 120 11.3 3-6 R-6 100 34 17 2.6 100 11.4 3-7 R-7 105 35 17 2.7 120 11.2 3-8 R-8 100 36 17 2.6 110 10.8 3-9 R-9 100 35 17 2.7 110 11.4 3-10 R-10 100 34 18 2.7 100 11.3 3-11 R-11 105 34 18 2.8 100 11.1 3-12 R-12 100 34 17 2.7 110 11.1 3-13 R-13 95 35 16 2.8 110 10.9 3-14 R-14 100 36 17 2.7 110 10.8 3-15 R-15 100 35 16 2.6 100 11.1 3-16 R-16 100 35 17 2.6 110 11.2 3-17 R-17 100 36 17 2.8 120 11.2 3-18 R-18 100 35 18 2.6 110 11.7 3-19 R-19 100 36 16 2.6 100 11.5 3-20 R-20 100 35 17 2.5 100 11.6 3-21 R-21 100 36 18 2.6 120 11.3 3-22 R-22 105 34 17 2.7 100 11.1 3-23 R-23 100 35 18 2.5 110 11.4 3-24 R-24 100 36 16 2.6 120 10.7 3-25 R-25 105 34 17 2.7 110 11.2 3-26

R-26 100 35 17 2.6 110 11.2 3-27 R-27 95 36 17 2.8 100 10.8 3-28 R-28 105 35 17 2.6 120 11.1 3-29 R-29 100 35 17 2.6 100 11.3 3-30 R-30 95 35 18 2.6 110 11.1

TABLE-US-00004 TABLE 4 Resist PEB temp. Eop EL LWR DOF Collapse limit composition (° C.) (mJ/cm.sup.2) (%) (nm) (nm) (nm) Comparative 2-1 CR-1 100 41 12 3.4 70 14.3 Example 2-2 CR-2 100 40 14 3.1 80 13.1 2-3 CR-3 105 41 14 3.2 70 13.3 2-4 CR-4 100 39 13 3.1 80 13.2 2-5 CR-5 100 41 14 3.0 90 13.4 2-6 CR-6 100 40 13 3.2 90 13.2 2-7 CR-7 100 42 13 3.3 70 12.7 2-8 CR-8 100 41 14 3.1 80 12.5 2-9 CR-9 105 40 14 3.0 70 13.2 2-10 CR-10 100 39 13 3.2 90 13.1 2-11 CR-11 100 41 14 3.1 80 12.9 2-12 CR-12 100 40 13 3.4 80 12.7 2-13 CR-13 100 38 13 3.5 80 13.1 2-14 CR-14 95 41 14 3.2 70 12.8 2-15 CR-15 105 40 14 3.5 90 13.2 2-16 CR-16 95 39 14 3.4 70 12.5 2-17 CR-17 100 40 13 3.2 80 13.1 2-18 CR-18 100 41 14 3.1 80 12.4 2-19 CR-19 100 42 13 3.3 90 12.7 2-20 CR-20 100 40 14 3.4 80 12.5

[0300] It is demonstrated in Tables 3 and 4 that chemically amplified resist compositions comprising quenchers within the scope of the invention exhibit a high sensitivity and improved values of EL, LWR and DOF. Small values of collapse limit attest that in forming a small-size pattern, the pattern is resistant to collapse. The resist compositions are useful in the EUV lithography process.

#### [5] EUV Lithography Test 2

Examples 4-1 to 4-30 and Comparative Examples 3-1 to 3-20

[0301] Each of the chemically amplified resist compositions (R-1 to R-30, CR-1 to CR-20) was spin coated on a silicon substrate having a 20-nm coating of silicon-containing spin-on hard mask SHB-A940 (Shin-Etsu Chemical Co., Ltd., silicon content 43 wt %) and prebaked on a hotplate at 105° C. for 60 seconds to form a resist film of 50 nm thick. Using an EUV scanner NXE3400 (ASML, NA 0.33, 6 0.9/0.6, quadrupole illumination), the resist film was exposed to EUV through a mask bearing a hole pattern having a pitch of 46 nm +20% bias (on-wafer size). The resist film was baked (PEB) on a hotplate at the temperature shown in Tables 5 and 6 for 60 seconds and developed in a 2.38 wt % TMAH aqueous solution for 30 seconds to form a hole pattern having a size of 23 nm.

[0302] The pattern as developed was observed under CD-SEM (CG6300, Hitachi High-Technologies Corp.). The dose (mJ/cm.sup.2) at which a pattern with a hole size of 23 nm was printed was determined as an index of sensitivity. The size of 50 holes was measured, from which a 3-fold value (36) of the standard deviation (6) was determined as a dimensional variation (or CDU). The results are shown in Tables 5 and 6.

TABLE-US-00005 TABLE 5 Resist PEB temp. Eop CDU composition (° C.) (mJ/cm.sup.2) (nm) Example 4-1 R-1 90 23 2.3 4-2 R-2 90 25 2.4 4-3 R-3 95 24 2.5 4-4 R-4 90 25 2.4 4-5 R-5 90 25 2.5 4-6 R-6 90 25 2.5 4-7 R-7 95 25 2.5 4-8 R-8 95 23 2.4 4-9 R-9 90 24 2.3 4-10 R-10 95 24 2.4 4-11 R-11 95 25 2.6 4-12 R-12 90 24 2.5 4-13 R-13 90 25 2.4 4-14 R-14 95 25 2.4 4-15 R-15 95 24 2.6 4-16 R-16 85 24 2.3 4-17 R-17 95 25 2.5 4-18 R-18 90 25 2.5 4-19 R-19 95 25 2.4 4-20 R-20 90 25 2.5 4-21 R-21 90 24 2.5 4-22 R-22 90 25 2.5 4-23 R-23 95 24 2.5 4-24 R-24 90 24 2.6 4-25 R-25 90 26 2.5 4-26 R-26 85 24 2.4 4-27 R-27 95 24 2.3 4-28 R-28 90 23 2.4 4-29 R-29 90 25 2.3 4-30 R-30 95 25 2.4

TABLE-US-00006 TABLE 6 Resist PEB temp. Eop CDU composition (° C.) (mJ/cm.sup.2) (nm) Comparative 3-1 CR-1 90 31 3.4 Example 3-2 CR-2 90 29 3 3-3 CR-3 95 29 2.8 3-4 CR-4 90 28 2.8 3-5 CR-5 95 30 3.1 3-6 CR-6 85 29 3.1 3-7 CR-7 90 28 2.8 3-8 CR-8 90 29 2.9 3-9 CR-9 90 30 3.2 3-10 CR-10 95 29 2.8 3-11 CR-11 90 28 3.1 3-12 CR-12 90 29 3 3-13 CR-13 95 31 2.9 3-14 CR-14 90 29 3.2 3-15 CR-15 90 30 3.2 3-16 CR-16 90 28 3.1 3-17 CR-17 95 28 3 3-18 CR-18 90 28 2.8 3-19 CR-19 85 30 2.9 3-20 CR-20 90 29 2.9

[0303] It is demonstrated in Tables 5 and 6 that chemically amplified resist compositions within the scope of the invention exhibit a high sensitivity and satisfactory CDU.

[0304] Japanese Patent Application No. 2024-022661 is incorporated herein by reference. Although some preferred embodiments have been described, many modifications and variations may be

made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

## Claims

1. An onium salt consisting of an aromatic carboxylic acid anion including a partial structure having iodine and a cyclic ether structure and an onium cation.
2. The onium salt of claim 1 having the formula (1): ##STR00534## wherein  $n_1$  is 0 or 1,  $n_2$  is an integer of 1 to 4,  $n_3$  is an integer of 1 to 4,  $n_4$  is an integer of 0 to 3,  $n_2+n_3+n_4$  is from 2 to 5 when  $n_1=O$ ,  $n_2+n_3+n_4$  is from 2 to 7 when  $n_1=1$ ,  $W_{sup}.A$  is a  $C_{sub}.2-C_{sub}.10$  group containing a cyclic ether structure,  $R_{sup}.1$  is halogen exclusive of iodine, or a  $C_{sub}.1-C_{sub}.20$  hydrocarbyl group which may contain a heteroatom, and when  $n_4$  is 2 or 3, a plurality of  $R_{sup}.1$  may bond together to form a ring with the carbon atoms on the aromatic ring to which they are attached, some  $-CH_{sub}.2-$  in the ring may be replaced by  $-O-$  or  $-S-$ ,  $L_{sup}.A$  and  $L_{sup}.B$  are each independently a single bond, ether bond, thioether bond, ester bond, amide bond, sulfonate ester bond, carbonate bond or carbamate bond,  $X_{sup}.L$  is a single bond or a  $C_{sub}.1-C_{sub}.40$  hydrocarbylene group which may contain a heteroatom, and  $Z_{sup}.+$  is an onium cation.
3. The onium salt of claim 2 wherein  $L_{sup}.A$  is an ether bond or thioether bond.
4. The onium salt of claim 2 wherein  $W_{sup}.A$  is an optionally substituted oxirane ring, optionally substituted oxetane ring, optionally substituted tetrahydrofuran ring or optionally substituted tetrahydropyran ring.
5. The onium salt of claim 2 wherein  $Z_{sup}.+$  is a sulfonium cation having the formula (cation-1), iodonium cation having the formula (cation-2) or ammonium cation having the formula (cation-3): ##STR00535## wherein  $R_{sup}.ct1$  to  $R_{sup}.ct9$  are each independently halogen or a  $C_{sub}.1-C_{sub}.30$  hydrocarbyl group which may contain a heteroatom, any two of  $R_{sup}.ct1$  to  $R_{sup}.ct3$  may bond together to form a ring with the sulfur atom to which they are attached, and any two of  $R_{sup}.ct6$  to  $R_{sup}.ct9$  may bond together to form a ring with the nitrogen atom to which they are attached.
6. A quencher in the form of the onium salt of claim 1.
7. A chemically amplified resist composition comprising the quencher of claim 6.
8. The resist composition of claim 7, further comprising a base polymer comprising repeat units having the formula (a1): ##STR00536## wherein  $R_{sup}.A$  is hydrogen, fluorine, methyl or trifluoromethyl,  $X_{sup}.1$  is a single bond, phenylene group, naphthylene group or  $*-C(=O)-O-X_{sup}.11-$ , the phenylene or naphthylene group may be substituted with an optionally fluorinated  $C_{sub}.1-C_{sub}.10$  alkoxy moiety or halogen,  $X_{sup}.11$  is a  $C_{sub}.1-C_{sub}.10$  saturated hydrocarbylene group which may contain a hydroxy moiety, ether bond, ester bond or lactone ring, or phenylene or naphthylene group, \* designates a point of attachment to the carbon atom in the backbone, and  $AL_{sup}.1$  is an acid labile group.
9. The resist composition of claim 8 wherein the base polymer further comprises repeat units having the formula (a2): ##STR00537## wherein  $R_{sup}.A$  is hydrogen, fluorine, methyl or trifluoromethyl,  $X_{sup}.2$  is a single bond or  $*-C(=O)-O-$ , \* designates a point of attachment to the carbon atom in the backbone,  $R_{sup}.11$  is halogen, cyano, a  $C_{sub}.1-C_{sub}.20$  hydrocarbyl group which may contain a heteroatom, a  $C_{sub}.1-C_{sub}.20$  hydrocarbyloxy group which may contain a heteroatom, a  $C_{sub}.2-C_{sub}.20$  hydrocarbylcarbonyl group which may contain a heteroatom, a  $C_{sub}.2-C_{sub}.20$  hydrocarbylcarbonyloxy group which may contain a heteroatom, or a  $C_{sub}.2-C_{sub}.20$  hydrocarbyloxycarbonyl group which may contain a heteroatom,  $AL_{sup}.2$  is an acid labile group, and  $a$  is an integer of 0 to 4.
10. The resist composition of claim 8 wherein the base polymer further comprises repeat units having the formula (b1) or (b2): ##STR00538## wherein  $R_{sup}.A$  is each independently hydrogen,



fluorine, methyl or trifluoromethyl, Y.sup.1 is a single bond or \*—C(=O)—O—, \* designates a point of attachment to the carbon atom in the backbone, R.sup.21 is hydrogen or a C.sub.1-C.sub.20 group containing at least one structure selected from the group consisting of hydroxy other than phenolic hydroxy, cyano, carbonyl, carboxy, ether bond, ester bond, sulfonate ester bond, carbonate bond, lactone ring, sultone ring and carboxylic anhydride (—C(=O)—O—C(=O)—), R.sup.22 is halogen, hydroxy, nitro, cyano, a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, a C.sub.1-C.sub.20 hydrocarbyloxy group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyl group which may contain a heteroatom, a C.sub.2-C.sub.20 hydrocarbylcarbonyloxy group which may contain a heteroatom, or a C.sub.2-C.sub.20 hydrocarbyloxycarbonyl group which may contain a heteroatom, b is an integer of 1 to 4, c is an integer of 0 to 4, and b+c is from 1 to 5.

**11.** The resist composition of claim 8 wherein the base polymer further comprises repeat units of at least one type selected from repeat units having the formulae (c1) to (c4): ##STR00539## wherein R.sup.A is each independently hydrogen, fluorine, methyl or trifluoromethyl, Z.sup.1 is a single bond or optionally substituted phenylene group, Z.sup.2 is a single bond, \*\*—C(=O)—O—Z.sup.21—, \*\*—C(=O)—NH—Z.sup.21—, or \*\*—O—Z.sup.21—, Z.sup.21 is a C.sub.1-C.sub.6 aliphatic hydrocarbylene group, phenylene group or a divalent group obtained by combining the foregoing, which may contain halogen, a carbonyl moiety, ester bond, ether bond or hydroxy moiety, Z.sup.3 is a single bond, ether bond, ester bond, amide bond, sulfonate ester bond, sulfonamide bond, carbonate bond or carbamate bond, Z.sup.4 is a single bond, or a C.sub.1-C.sub.6 aliphatic hydrocarbylene group, phenylene group or a divalent group obtained by combining the foregoing, which may contain halogen, carbonyl moiety, ester bond, ether bond or hydroxy moiety, Z.sup.5 is each independently a single bond, optionally substituted phenylene group, naphthylene group, or \*—C(=O)—O—Z.sup.5, Z.sup.51 is a C.sub.1-C.sub.10 aliphatic hydrocarbylene group which may contain halogen, hydroxy moiety, ether bond, ester bond or lactone ring, or phenylene or naphthylene group, Z.sup.6 is a single bond, ether bond, ester bond, amide bond, sulfonate ester bond, sulfonamide bond, carbonate bond or carbamate bond, Z.sup.7 is each independently a single bond, \*\*\*—Z.sup.71—C(=O)—O—, \*\*\*—C(=O)—NH—Z.sup.71—, or \*\*\*—O—Z.sup.71—, Z.sup.71 is a C.sub.1-C.sub.20 hydrocarbylene group which may contain a heteroatom, Z.sup.8 is each independently a single bond, \*\*\*\*—Z.sup.81—C(=O)—O—, \*\*\*\*—C(=O)—NH—Z.sup.81—, or \*\*\*\*—O—Z.sup.81—, Z.sup.81 is a C.sub.1-C.sub.20 hydrocarbylene group which may contain a heteroatom, Z.sup.9 is a single bond, methylene, ethylene, phenylene, fluorinated phenylene, trifluoromethyl-substituted phenylene, \*—C(=O)—O—Z.sup.91—, \*—C(=O)—N(H)—Z.sup.9—, or \*—O—Z.sup.91, Z.sup.91 is a C.sub.1-C.sub.6 aliphatic hydrocarbylene group, phenylene group, fluorinated phenylene group or trifluoromethyl-substituted phenylene group, which may contain a carbonyl moiety, ester bond, ether bond or hydroxy moiety, \* designates a point of attachment to the carbon atom in the backbone, \*\* designates a point of attachment to Z.sup.1, \*\*\* designates a point of attachment to Z.sup.6, \*\*\*\* designates a point of attachment to Z.sup.7, R.sup.31 and R.sup.32 are each independently a C.sub.1-C.sub.20 hydrocarbyl group which may contain a heteroatom, R.sup.31 and R.sup.32 may bond together to form a ring with the sulfur atom to which they are attached, L.sup.1 is a single bond, ether bond, ester bond, carbonyl group, sulfonate ester bond, carbonate bond or carbamate bond, Rf.sup.1 and Rf.sup.2 are each independently fluorine or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group, Rf.sup.3 and Rf.sup.4 are each independently hydrogen, fluorine, or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group, Rf.sup.5 and Rf.sup.6 are each independently hydrogen, fluorine, or a C.sub.1-C.sub.6 fluorinated saturated hydrocarbyl group, excluding that all Rf.sup.5 and Rf.sup.6 are hydrogen at the same time, M.sup.— is a non-nucleophilic counter ion, A.sup.+ is an onium cation, and d is 0, 1, 2 or 3.

**12.** The resist composition of claim 7, further comprising an organic solvent.

**13.** The resist composition of claim 7, further comprising a photoacid generator capable of

generating a strong acid.

**14.** The resist composition of claim 7, further comprising another quencher other than the quencher.

**15.** The resist composition of claim 7, further comprising a surfactant.

**16.** A pattern forming process comprising the steps of applying the chemically amplified resist composition of claim 7 onto a substrate to form a resist film thereon, exposing the resist film to high-energy radiation, and developing the exposed resist film in a developer.

**17.** The pattern forming process of claim 16 wherein the high-energy radiation is KrF excimer laser radiation, ArF excimer laser radiation, EB or EUV of wavelength 3 to 15 nm.

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