

CHEMICAL AMPLIFICATION TYPE POSITIVE RESIST COMPOSITIONS AND
SULFONIUM SALTS

BACKGROUND OF THE INVENTION

5 The present invention relates to a chemical amplifying type positive resist composition used in the minute processing of a semiconductor and a novel compound usable as an acid generator in said resist composition.

 In general, a lithography process using a resist
10 composition has been adopted in the minute processing of a semiconductor. In lithography, the resolution can be improved with a decrease in wavelength of exposure light in principle as expressed by the equation of Rayleigh's diffraction limited. A g-line with a wavelength of 436 nm, an i-line with a wavelength
15 of 365 nm, and a KrF excimer laser with a wavelength of 248 nm have been adopted as exposure light sources for lithography used in the manufacture of a semiconductor. Thus, the wavelength has become shorter year by year. An ArF excimer laser having a wavelength of 193 nm is considered to be promising as a
20 next-generation exposure light source, and some of resists for ArF excimer laser are being made practical.

 A lens used in an ArF excimer laser exposure machine or an exposure machine using a light -source of shorter wave-length has a shorter lifetime as compared with lenses for conventional
25 exposure light sources. Accordingly, the shorter time required for exposure to ArF excimer laser light is desirable. For this reason, it is necessary to enhance the sensitivity of a resist. Consequently, there has been used a so-called chemical

amplifying type resist, which utilizes the catalytic action of an acid generated due to exposure, and contains a resin having a group cleavable by the action of acid.

It is known that, desirably, resins used in a resist for ArF excimer laser exposure have no aromatic ring in order to ensure the transmittance of the resist, but have an alicyclic ring in place of an aromatic ring in order to impart a dry etching resistance thereto. Various kinds of resins such as those described in Journal of Photopolymer Science and Technology, Vol. 9, No. 3, pages 387-398 (1996) by D. C. Hofer, are heretofore known as such resins.

S. Takechi et al., Journal of Photopolymer Science and Technology, Vol. 9, No. 3, pages 475-487 (1996), and JP-A-9-73173 reported that, when a polymer or copolymer of 2-methyl-2-adamantyl methacrylate was used as the resin in a chemical amplifying type resist, 2-methyl-2-adamantyl was cleaved by the action of an acid to act as an positive type and a high dry etching resistance, a high resolution and a good adhesion to a substrate could be obtained. In addition, JP-A-10-274852 reported that the adhesion to a substrate was improved by using a resin having a butyrolactone residue in a part of polymerization units as the resin constituting a chemical amplification type positive resist composition. Further, JP-A-10-319595 described a resist composition containing a resin having a γ -butyrolactone-3-yl residue as a protective group for carboxyl group.

On the other hand, since the chemical amplification type resists utilizes the action of an acid, a problem arises that

profiles are liable to be bottom-tailed by deactivation of the acid when the substrate is of a basic nature. It is known that this problem can be resolved by adding a much amount of a basic quencher substance. Addition of a much amount of such quencher substance, however, results in decrease of the sensitivity of the resist. In addition, in ArF-exposure, a resist is often applied on a substrate having a low reflection such as an organic or inorganic anti-reflective layer. When such a substrate having a low reflection is used, the profile of the resist generally deteriorated in a taper shape due to light absorption, although dimension uniformity is effectively improved.

One possible mean for lowering the light absorption is to reduce the amount of the acid generator. In this case, however, the sensitivity is generally decreased. Another mean for lowering the light absorption is to use an aliphatic sulfonium salt having a high transparency such as those described in JP-A-7-25846, JP-A-7-28237, JP-A-7-92675 and JP-A-8-27102. In the cases of these known aliphatic sulfonium salts, however, a sufficient resolution cannot be obtained and a problem that the profile on a basic substrate becomes bottom-tailed shape cannot be dissolved. Therefore, the chemical amplification type resists containing a conventional acid generator had a problem that performances, particularly the profile, are varied depending on the kind of the substrate.

An object of the present invention is to provide a chemical amplification type positive resist composition, which contains a resin component and an acid generator, which is suitable to use in excimer laser lithography with ArF, KrF or the like,

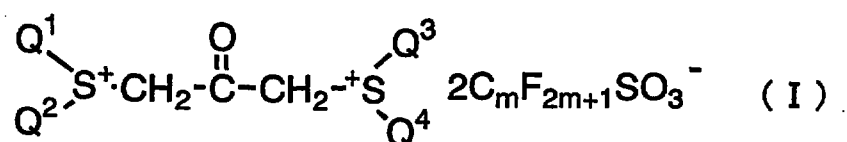
particularly in lithography with a light having a wavelength of 220 nm or lower, for example, ArF excimer laser light, and which is superior in sensitivity and resolution conferring a good profile.

5 Another object of the invention is to provide a compound useful as an acid generator in such a chemical amplification type positive resist composition.

The present inventors have found the fact that the transmittance and the resolution can be improved by using a
10 combination of certain kinds of acid generators. Thus, the present invention has been completed.

SUMMARY OF THE INVENTION

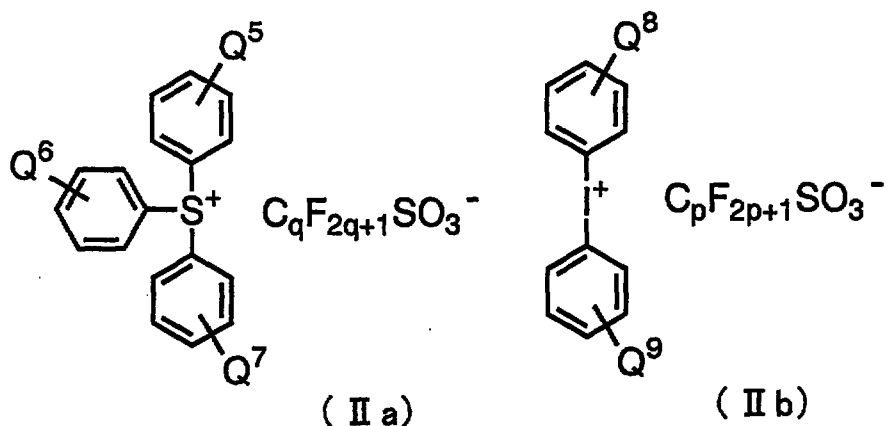
The present invention provides a chemical amplifying type
15 positive resist composition comprising an aliphatic sulfonium salt represented by the following formula (I):



wherein either Q^1 , Q^2 , Q^3 and Q^4 independently represent an alkyl group having 1 to 6 carbon atoms or a cycloalkyl group having
20 3 to 10 carbon atoms, or Q^1 and Q^2 and/or Q^3 and Q^4 independently form, together with the adjacent sulfur atom, a heterocyclic group which has 2 to 8 carbon atoms and which may further have an oxygen atom or a sulfur atom, and m represents an integer of 1 to 8;

25 at least one onium salt selected from the group consisting of

a triphenylsulfonium salt represented by the following formula (IIa) and a diphenyliodonium salt represented by the following formula (IIb):



wherein Q^5 , Q^6 , Q^7 , Q^8 and Q^9 independently represent a hydrogen atom, a hydroxyl group, an alkyl group having 1 to 6 carbon atoms or an alkoxy group having 1 to 6 carbon atoms, and p and q represent integer of 1 to 8; and a resin which contains a polymerization unit having a group unstable to an acid, and which is insoluble in alkali by itself but becomes soluble in alkali by the action of an acid.

The aliphatic sulfonium salt represented by the above formula (I) is a novel compound never described in literature. Therefore, the invention also provides the sulfonium compound represented by the above formula (I).

DETAILED DESCRIPTION OF THE INVENTION

The acid generator used in the chemical amplification type resist composition is a substance that decomposes to generate an acid by acting a radiation such as a light or an electronic ray on the substance itself or a resist composition containing the substance. In the resist composition of the

invention, both of an aliphatic sulfonium salt represented by the above formula (I), and at least one onium salt selected from the group consisting of a triphenylsulfonium salt represented by the above formula (IIa) and a diphenyliodonium salt represented by the above formula (IIb). Such acid generators are used together.

In the formula (I), either Q^1 , Q^2 , Q^3 and Q^4 independently represent an alkyl group having 1 to 6 carbon atoms or a cycloalkyl group having 3 to 10 carbon atoms. Alternatively, Q^1 , Q^2 and the sulfur atom bonding to them, and/or Q^3 , Q^4 and the sulfur atom bonding to them may form a heterocyclic group which has 2 to 8 carbon atoms and which may further have an oxygen atom or a sulfur atom. When the alkyl group has 3 or more carbon atoms, the group can be straight-chained or branched. Typical examples of the alkyl group include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like. Typical examples of the cycloalkyl group include cyclopentyl, cyclohexyl, cycloheptyl and the like. Typical examples of the heterocyclic groups formed by Q^1 , Q^2 and the sulfur atom bonding to them, and those formed by Q^3 , Q^4 and the sulfur atom bonding to them include ethylene sulfide, trimethylene sulfide, tetrahydrothiophene, tetrahydrothiopyran, thioxane, dithian, tetrahydrothiophene-3-one, tetrahydrothiopyran-4-one and the like. In the formula (I), m representing the number of carbon atoms in an alkane moiety constituting a perfluoroalkanesulfonate anion is an integer of 1 to 8. Typical examples of the moiety corresponding to the perfluoroalkanesulfonate anion include

These reactions are carried out in an appropriate solvent, such as acetone, acetonitrile, nitromethane or the like. The sulfide compound of the formula (A2) is used in an amount preferably of 1.8 to 3 moles, more preferably of 2.0 to 2.2 moles, based on 1 mole of the dihalogenoacetone corresponding to the formula (A1). The metal salt of a perfluoroalkanesulfonic acid of the formula: $C_mF_{2m+1}SO_3M$ may be used preferably in an amount of 0.8 to 1.2 mole, more preferably 0.9 to 1.1 mole, based on 1 mole of the sulfide compound of the formula (A2) used for the production of the sulfonium halide of the formula (B). After completion of the reaction, the aliphatic sulfonium salt can be obtained by removing the generated metal halide salt by filtration or the like and subjecting the solution to a post-treatment such as concentration, recrystallization or others.

Specific examples of the aliphatic sulfonium salt represented by the formula (I) include the following compounds:

(2-oxo-1,3-propanediyl)bis(dimethylsulfonium)
bis(trifluoromethanesulfonate),

(2-oxo-1,3-propanediyl)bis(dimethylsulfonium)
bis(perfluorobutanesulfonate),

(2-oxo-1,3-propanediyl)bis(dimethylsulfonium)
bis(perfluorooctanesulfonate),

(2-oxo-1,3-propanediyl)bis(diethylsulfonium)
bis(perfluorobutanesulfonate),

(2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
bis(trifluoromethanesulfonate),

(2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
bis(perfluorobutanesulfonate),

(2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
 bis(perfluorooctanesulfonate),
 (2-oxo-1,3-propanediyl)bis(diisopropylsulfonium)
 bis(perfluorobutanesulfonate),
 5 (2-oxo-1,3-propanediyl)bis(tert-butylmethylsulfonium
) bis(perfluorobutanesulfonate),
 (2-oxo-1,3-propanediyl)bis(cyclohexylmethylsulfonium
) bis(perfluorobutanesulfonate),
 1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiopheniu
 10 m) bis(trifluoromethanesulfonate),
 1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiopheniu
 m) bis(perfluorobutanesulfonate),
 1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiopheniu
 m) bis(perfluorooctanesulfonate),
 15 1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiopyrani
 um) bis(perfluorobutanesulfonate),
 1,1'-(2-oxo-1,3-propanediyl)bis(1,4-thioxolanium)
 bis(perfluorobutanesulfonate),
 1,1'-(2-oxo-1,3-propanediyl)bis(4-oxotetrahydrothiop
 20 yranium) bis(perfluorobutanesulfonate) and the like.

In the present invention, at least one onium salt selected
 from the group consisting of compounds of the formula (IIa)
 and the formula (IIb) is used as the acid generator together
 with the aliphatic sulfonium salt of the formula (I). In these
 25 onium salts, Q⁵, Q⁶, Q⁷, Q⁸ and Q⁹ respectively represent a hydrogen
 atom, a hydroxyl group, an alkyl group having 1 to 6 carbon
 atoms or an alkoxy group having 1 to 6 carbon atoms. When the
 alkyl group or the alkoxy group has 3 or more carbon atoms,

such group can be straight-chained or branched. Typical examples of the alkyl group include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like. Typical examples of the alkoxy group include methoxy, ethoxy, propoxy, butoxy and the like. In the formulae (IIa) and (IIb), p and q representing the numbers of carbon atoms in alkanemoieties constituting perfluoroalkanesulfonate anion are integers of 1 to 8.

The triphenylsulfonium salt represented by the formula (IIa) and the diphenyliodonium salt represented by the formula (IIb) can be commercial products thereof, if available. Otherwise, they can be produced according to the conventional process. As to the process for producing the triphenylsulfonium salt (IIa), following processes can be exemplified: a process in which the corresponding triphenylsulfoniumbromide is reacted with a silver perfluoroalkanesulfonate, a process in which the corresponding diphenylsulfoxide is reacted with a benzene compound and a perfluoroalkanesulfonic acid in the presence of trifluoroacetic anhydride according to the description in Chemical and Pharmaceutical Bulletin, Vol. 29, 3753 (1981), a process in which a corresponding aryl Grignard reagent is reacted with thionyl chloride, then with a triorganosilyl halide to give a triarylsulfonium halide, followed by a reaction with a silver perfluoroalkanesulfonate according to the description in JP-A-8-311018, and so on. Compounds of the formula (IIa) wherein at least one of Q^5 , Q^6 and Q^7 is hydroxyl group can be produced by treating a triphenylsulfonium salt having a tert-butoxy group on the benzene ring with a sulfonic acid having

the same anion as that of the triphenylsulfonium salt to eliminate the tert-butyl group according to the description in the same JP-A-8-311018.

As to the process for producing the diphenyliodonium salt (IIb), following processes can be exemplified: a process in which iodyl sulfate is reacted with a corresponding aryl compound, followed by addition of a perfluoroalkanesulfonic acid according to the description in Journal of American Chemical Society, Vol. 81, 342 (1959), a process in which concentrated sulfuric acid is added dropwise to a mixture of a corresponding aryl compound, acetic anhydride and potassium iodate to cause a reaction, followed by addition of a perfluoroalkanesulfonic acid, a process in which a reaction product obtained by adding iodine and trifluoroacetic acid to a mixed solution of acetic anhydride and fuming nitric acid is reacted with a corresponding aryl compound, followed by addition of a perfluoroalkanesulfonic acid, and so on.

Specific examples of the triphenylsulfonium salt corresponding to the formula (IIa) and the diphenyliodonium salt corresponding to the formula (IIb) include the following compounds:

triphenylsulfonium trifluoromethanesulfonate,
triphenylsulfonium perfluorobutanesulfonate,
triphenylsulfonium perfluorooctanesulfonate,
4-methylphenyldiphenylsulfonium
trifluoromethanesulfonate,
4-methylphenyldiphenylsulfonium
perfluorobutanesulfonate,

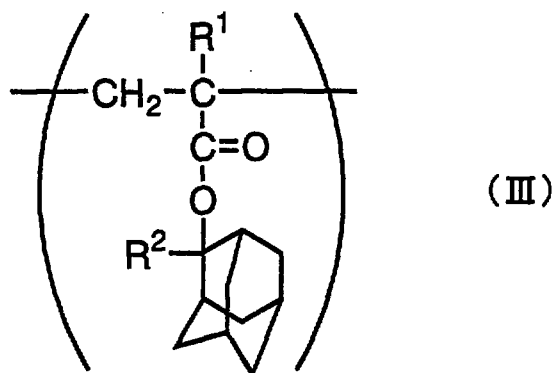
4-hydroxyphenyldiphenylsulfonium
 perfluorobutanesulfonate,
 4-methoxyphenyldiphenylsulfonium
 perfluorobutanesulfonate,
 5 tris(4-methylphenyl)sulfonium
 perfluorobutanesulfonate,
 tris(4-methoxyphenyl)sulfonium
 perfluorobutanesulfonate,
 triphenylsulfonium perfluorooctanesulfonate,
 10 4-methylphenyldiphenylsulfonium
 perfluorooctanesulfonate,
 4-hydroxyphenyldiphenylsulfonium
 perfluorooctanesulfonate,
 4-methoxyphenyldiphenylsulfonium
 15 perfluorooctanesulfonate,
 tris(4-methylphenyl)sulfonium
 perfluorooctanesulfonate,
 tris(4-methoxyphenyl)sulfonium
 perfluorooctanesulfonate,
 20 diphenyliodonium perfluorobutanesulfonate,
 di(4-methoxyphenyl)iodonium perfluorooctanesulfonate,
 di(4-tert-butylphenyl)iodonium
 perfluorooctanesulfonate, and the like.

The resin component constituting the resist composition
 25 of the invention contains a polymerization unit having a group
 unstable to an acid. The resin for use in a chemical amplifying
 type positive resist is generally alkali-insoluble or hardly
 alkali-soluble by itself. However, a part of a group therein

is cleaved by the action of an acid, and the resin becomes alkali-soluble after the cleavage. The group unstable to an acid in the invention can be various groups conventionally known in the art. Examples of the group unstable to an acid include
5 various esters of carboxylic acid. Examples of the esters of carboxylic acid include alkyl esters such as methyl ester and tert-butyl ester, acetal type esters such as methoxymethyl ester, ethoxymethyl ester, 1-ethoxyethyl ester, 1-isobutoxyethyl ester, 1-isopropoxyethyl ester, 1-ethoxypropyl ester,
10 1-(2-methoxyethoxy)ethyl ester, 1-(2-acetoxyethoxy)ethyl ester, 1-[2-(1-adamantyloxy)ethoxy]ethyl ester, 1-[2-(1-adamantanecarbonyloxy)ethoxy]ethyl ester, tetrahydro-2-furyl ester and tetrahydro-2-pyranyl ester, alicyclic esters such as isobornyl ester and 2-alkyl-2-adamantyl
15 ester, and the like. Examples of the monomers leading these polymerization units having a carboxylic ester include (meth)acrylic monomer such as methacrylic ester and acrylic ester, and alicyclic monomers having a carboxylic ester bound thereto such as norbornenecarboxylic ester,
20 tricyclodecenecarboxylic ester and tetracyclodecenecarboxylic ester.

Among the polymerization unit having a group unstable to an acid, a polymerization unit of 2-alkyl-2-adamantyl (meth)acrylate is preferable from a viewpoint of resolution
25 of the resist containing it. This polymerization unit can be formed by opening the double bond of (meth)acrylic acid moiety in the 2-alkyl-2-adamantyl acrylate or 2-alkyl-2-adamantyl methacrylate, and is specifically represented by the following

formula (III):



wherein R^1 represents hydrogen or methyl and R^2 represents alkyl,

The polymerization unit of 2-alkyl-2-adamantyl

(meth)acrylate represented by the formula (III) ensures the

transmittance of a resist and contributes to the improvement
of dry etching resistance due to the presence of an adamantane

ring. Further, the 2-alkyl-2-adamantyl in this unit is cleaved

by the action of an acid. Hence, this unit contributes to the
enhancement of alkali-solubility after exposure to radiation

of a resist film. R^2 in the formula (I) is alkyl. This alkyl

may have, for example, about 1 to 8 carbon atoms. In general,

the alkyl is advantageously straight-chained, but it may be

branched when the number of carbons is 3 or more. Specific

examples of R^2 include methyl, ethyl, propyl, isopropyl, butyl

and the like. Among them, those having methyl or ethyl as R^2

are preferred for the improvement of adhesion between the resist

film and the substrate and for the improvement of resolution.

Specific examples of monomers leading the polymerization

unit of 2-alkyl-2-adamantyl (meth)acrylate represented by the

formula (III) include 2-methyl-2-adamantyl acrylate,

2-ethyl-2-adamantyl acrylate, 2-methyl-2-adamantyl

methacrylate, 2-ethyl-2-adamantyl methacrylate and the like.

The 2-alkyl-2-adamantyl (meth)acrylate can generally be produced by the reaction of a 2-alkyl-2-adamantanol or a metal salt thereof with an acrylic halide or methacrylic halide.

The resin defined in the invention can also contain another polymerization unit that is not cleaved or is hardly cleaved by the action of an acid in addition to a polymerization unit having a group unstable to an acid as described above. Examples of another possible polymerization unit include those derived from monomers having a free carboxylic acid group such as acrylic acid or methacrylic acid, those derived from aliphatic unsaturated dicarboxylic anhydride such as maleic anhydride or itaconic anhydride, those derived from 2-norbornene, those derived from (meth)acrylonitrile, those derived from various (meth)acrylic esters such as 2-hydroxyethyl (meth)acrylate, 3-hydroxy-1-adamantyl (meth)acrylate, (meth)acryloyloxy- γ -butyrolactone, and the like.

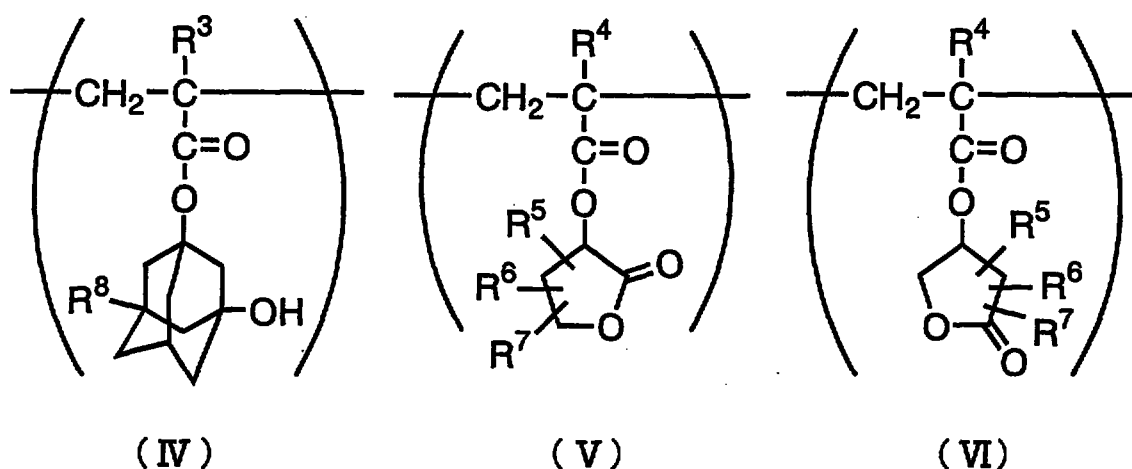
Particularly, the polymerization units of 3-hydroxy-1-adamantyl (meth)acrylate and polymerization units of (meth)acryloyloxy- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl are preferred from the viewpoint of adhesiveness of the resist film to the substrate. The polymerization unit of 3-hydroxy-1-adamantyl (meth)acrylate cited herein means a unit formed by opening the double bond of the (meth)acrylic acid moiety in the corresponding 3-hydroxy-1-adamantyl(meth)acrylate. The polymerization unit of (meth)acryloyloxy- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl herein means a unit formed by opening the double bond of the (meth)acrylic

acid moiety in α -(meth)acryloyloxy- γ -butyrolactone which is unsubstituted or alkyl-substituted in the lactone ring, or a unit formed by opening the double bond of the (meth)acrylic acid moiety in β -(meth)acryloyloxy- γ -butyrolactone which is

5 unsubstituted or alkyl-substituted in the lactone ring.

The polymerization units derived from 3-hydroxy-1-adamantyl(meth)acrylate, α -(meth)acryloyloxy- γ -butyrolactone which is unsubstituted or alkyl-substituted in the lactone ring, and

10 β -(meth)acryloyloxy- γ -butyrolactone which is unsubstituted or alkyl-substituted in the lactone ring can be represented, respectively, by the following formulae (IV), (V) and (VI):



wherein R^3 and R^4 independently represent hydrogen or methyl, R^5 , R^6 and R^7 independently represent hydrogen or alkyl and R^8

15 represents hydrogen or hydroxyl.

The 3-hydroxy-1-adamantyl (meth)acrylate for leading a unit of the formula (IV) is commercially available and can be produced, for example, by reacting the corresponding hydroxyadamantane with (meth)acrylic acid or a halide thereof.

20 The α - or β -(meth)acryloyloxy- γ -butyrolactone for leading a unit

of the formula (V) or (VI) can be produced by reacting acrylic acid or methacrylic acid with α - or β -bromo- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl, or by reacting an acrylic halide or methacrylic halide
5 with α - or β -hydroxy- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl.

All the polymerization unit of 3-hydroxy-1-adamantyl (meth)acrylate represented by the formula (IV), the polymerization unit of α -(meth)acryloyloxy- γ -butyrolactone
10 represented by the formula (V) and the polymerization unit of β -(meth)acryloyloxy- γ -butyrolactone represented by the formula (VI) have a high polarity and confer an improved adhesiveness between the resist film containing any of them to the substrate. In addition, these polymerization units also contribute to the
15 improvement of the resolution of the resist. Furthermore, the polymerization unit of 3-hydroxy-1-adamantyl (meth)acrylate contributes to the improvement of the dry etching resistance of a resist. Moreover, the polymerization unit of
20 β -methacryloyloxy- γ -butyrolactone contributes to the improvement of transmittance of the resist.

Examples of the monomers for leading the polymerization unit of 3-hydroxy-1-adamantyl (meth)acrylate represented by the formula (IV) include 3-hydroxy-1-adamantyl acrylate, 3-hydroxy-1-adamantyl methacrylate,
25 3,5-dihydroxy-1-adamantyl acrylate, 3,5-dihydroxy-1-adamantyl methacrylate and so on. In the formula (V) and the formula (VI), R^5 , R^6 and R^7 are respectively hydrogen or alkyl. This alkyl may have about 1 to 6 carbon atoms

and when the alkyl group has 3 or more carbon atoms, the group can be straight-chained or branched. Typical examples of the alkyl represented by R^5 , R^6 and R^7 include methyl, ethyl, propyl, butyl and the like. Examples of monomers for leading the
5 polymerization unit of α -(meth)acryloyloxy- γ -butyrolactone represented by the formula (V) include

α -acryloyloxy- γ -butyrolactone,

α -methacryloyloxy- γ -butyrolactone,

α -acryloyloxy- β,β -dimethyl- γ -butyrolactone,

10 α -methacryloyloxy- β,β -dimethyl- γ -butyrolactone,

α -acryloyloxy- α -methyl- γ -butyrolactone,

α -methacryloyloxy- α -methyl- γ -butyrolactone and the like.

Examples of monomers leading the polymerization unit of

β -(meth)acryloyloxy- γ -butyrolactone represented by the formula

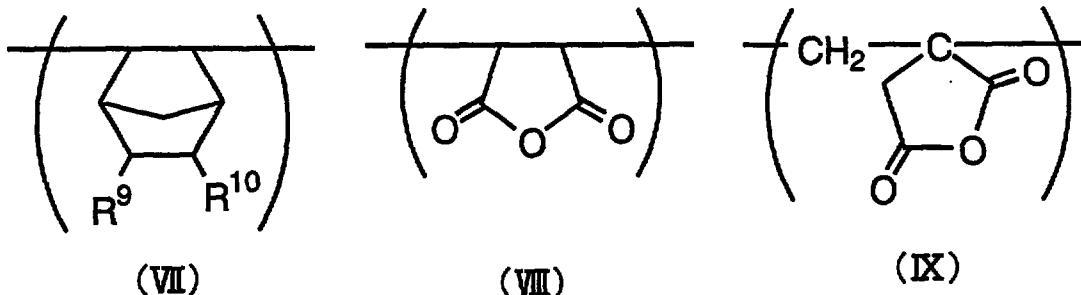
15 (VI) include β -acryloyloxy- γ -butyrolactone,

β -methacryloyloxy- γ -butyrolactone,

β -methacryloyloxy- α -methyl- γ -butyrolactone and the like.

Resins containing a polymerization unit of 2-norbornene have a strong structure, because they have an alicyclic ring
20 directly in the main chain. As the result, they are excellent in dry etching resistance. The polymerization unit of 2-norbornene can be introduced, for example, by a radical polymerization using an aliphatic unsaturated dicarboxylic anhydride such as maleic anhydride or itaconic anhydride
25 together with the corresponding 2-norbornene. Therefore, the polymerization unit of 2-norbornene is a unit formed by opening the double bond therein and can be represented by the formula (VII). The polymerization units of maleic anhydride and the

polymerization unit of itaconic anhydride as the polymerization units of the aliphatic unsaturated dicarboxylic anhydrides are units formed by opening the double bonds therein and can be represented by the formulae (VIII) and (IX).



5 In the formula (VII), either R^9 and R^{10} independently represent hydrogen, alkyl having 1 to 3 carbon atoms, hydroxyalkyl having 1 to 3 carbon atoms, carboxyl, cyano or the group: $-COOZ$ wherein Z is an alcohol residue, or R^9 and R^{10} may be combined together to form a carboxylic anhydride residue

10 represented by $-C(=O)OC(=O)-$. Specific examples of alkyl represented by R^9 or R^{10} include methyl, ethyl, propyl and the like. Specific examples of hydroxyalkyl represented by R^9 or R^{10} include hydroxymethyl, 2-hydroxyethyl and the like.

Examples of the alcohol residue represented by Z include alkyl

15 with about 1 to 8 carbon atoms, which is unsubstituted or substituted, 2-oxoxolane-3- or -4-yl and the like. Possible substituents on the alkyl include a hydroxyl group, an alicyclic hydrocarbon residue and the like. Specific examples of carboxylic ester group represented by $-COOZ$ include

20 methoxycarbonyl, ethoxycarbonyl, 2-hydroxyethoxycarbonyl, tert-butoxycarbonyl, 2-oxoxolane-3-yloxycarbonyl, 2-oxoxolane-4-yloxycarbonyl, 1,1,2-trimethylpropoxycarbonyl,

1-cyclohexyl-1-methylethoxycarbonyl,
1-(4-methylcyclohexyl)-1-methylethoxycarbonyl,
1-(1-adamantyl)-1-methylethoxycarbonyl and the like.

Examples of monomers for leading the polymerization unit
5 of formula (VII) include
2-norbornene, 2-hydroxy-5-norbornene,
5-norbornene-2-carboxylic acid, methyl
5-norbornene-2-carboxylate, t-butyl
5-norbornene-2-carboxylate, 1-cyclohexyl-1-methylethyl
10 5-norbornene-2-carboxylate,
1-(4-methylcyclohexyl)-1-methylethyl
5-norbornene-2-carboxylate,
1-(4-hydroxylcyclohexyl)-1-methylethyl
5-norbornene-2-carboxylate,
15 1-methyl-1-(4-oxocyclohexyl)ethyl
5-norbornene-2-carboxylate,
1-(1-adamantyl)-1-methylethyl 5-norbornene-2-carboxylate,
1-methylcyclohexyl 5-norbornene-2-carboxylate,
2-methyl-2-adamantyl 5-norbornene-2-carboxylate,
20 2-ethyl-2-adamantyl 5-norbornene-2-carboxylate,
2-hydroxyl-1-ethyl 5-norbornene-2-carboxylate,
5-norbornene-2-methanol
5-norbornene-2,3-dicarboxylic acid anhydride, and the like.

Depending on the kind of radiation for patterning exposure
25 and the kind of group unstable to an acid, it is generally
preferred that the resin used in the invention contains the
polymerization unit having a group unstable to an acid in a
range of 10 to 80% bymole based on the total resin. Particularly,

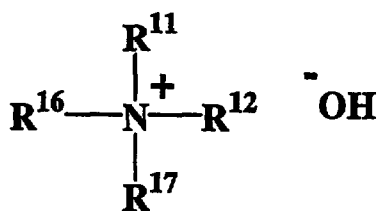
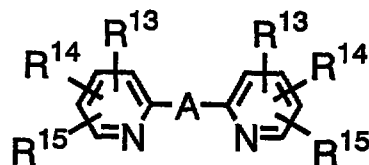
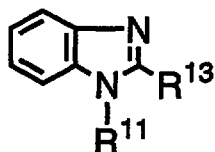
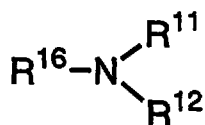
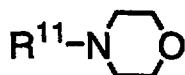
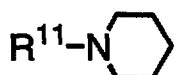
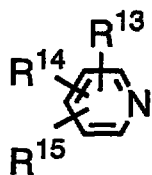
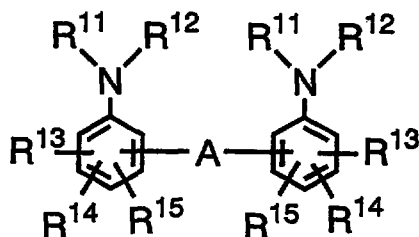
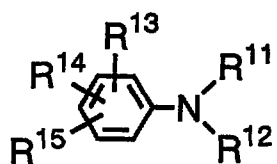
when the polymerization unit of 2-alkyl-2-adamantyl
(meth)acrylate represented by the formula (III) is used as the
group unstable to an acid, it is preferred that the unit exists
in 15% by mole or more based on the total resin. When, in addition
5 to the polymerization unit having a group unstable to an acid,
another polymerization unit hardly cleavable by the action of
an acid, such as the polymerization unit of
3-hydroxy-1-adamantyl (meth)acrylate represented by the
formula (IV), the polymerization unit of
10 α -(meth)acryloyloxy- γ -butyrolactone represented by the formula
(V), the polymerization unit of
 β -(meth)acryloyloxy- γ -butyrolactone represented by the formula
(VI), the polymerization unit of 2-norbornene represented by
the formula (VII), the polymerization unit of maleic anhydride
15 represented by the formula (VIII) and the polymerization unit
of itaconic anhydride represented by the formula (IX) as the
polymerization units of the aliphatic unsaturated dicarboxylic
anhydrides, are present, it is preferred that these units exist
within a range of 20 to 90% by mole in total based on the total
20 resin.

When a copolymer containing the polymerization unit of
3-hydroxy-1-adamantyl (meth)acrylate represented by the
formula (IV) and/or the polymerization unit of
 α -(meth)acryloyloxy- γ -butyrolactone represented by the formula
25 (V) as well as the polymerization unit of 2-norbornene
represented by the formula (VII) and the polymerization unit
of the aliphatic unsaturated dicarboxylic anhydrides
represented by the formula (VIII) or (IX) together with the

polymerization unit having a group unstable to an acid containing a unit of 2-alkyl-2-adamantyl (meth)acrylate represented by the formula (III) is desired, it is usual to copolymerize a monomer mixture containing 10 to 80% by mole of a monomer having a group unstable to an acid, particularly 15% by mole or more of 2-alkyl-2-adamantyl (meth)acrylate for leading a unit of the formula (III), and 20 to 90% by mole in total of 3-hydroxy-1-adamantyl (meth)acrylate for leading the unit of the formula (IV) and/or α -(meth)acryloyloxy- γ -butyrolactone for leading the unit of the formula (V) as well as a 2-norbornene compound for leading the unit of the formula (VII) and a monomer for leading the polymerization unit of aliphatic unsaturated dicarboxylic anhydride for leading the unit of the formula (VIII) or (IX). When a 2-norbornene compound and an aliphatic unsaturated dicarboxylic anhydride are used as monomers for copolymerization, it is preferred to use them in excess in view of the fact that these have a tendency of hardly polymerizing. Likewise, when a copolymer containing a polymerization unit of β -(meth)acryloyloxy- γ -butyrolactone represented by the formula (VI) together with a polymerization unit having a group unstable to an acid is desired, it is advantageous to polymerize a monomer mixture containing 10 to 80% by mole of a monomer having a group unstable to an acid and 20 to 90% by mole of β -(meth)acryloyloxy- γ -butyrolactone for leading the unit of the formula (VI).

It is also known that, generally in a chemical amplifying type positive resist composition, performance deterioration due to the deactivation of an acid associated with leaving after

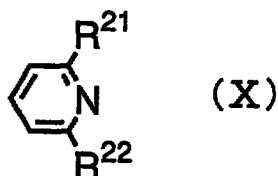
exposure can be reduced by adding a basic compound, especially a basic nitrogen-containing organic compound such as amines as a quencher. It is also preferable in the present invention that such basic compounds are added. Concrete examples of the
 5 basic compounds to be used as quenchers include the ones represented by the following formulae:



wherein R¹¹, R¹² and R¹⁷ represent, independently each other,
 10 hydrogen, cycloalkyl, aryl or alkyl which may be optionally

substituted with a hydroxyl, amino which may be optionally substituted with alkyl having 1 to 6 carbon atoms, or alkoxy having 1 to 6 carbon atoms; R^{13} , R^{14} and R^{15} , which are same or different from each other, represent hydrogen, cycloalkyl, aryl, alkoxy or alkyl which may be optionally substituted with a hydroxyl, amino which may be optionally substituted with alkyl having 1 to 6 carbon atoms, or alkoxy having 1 to 6 carbon atoms; R^{16} represents cycloalkyl or alkyl which may be optionally substituted with a hydroxyl, amino which may be optionally substituted with alkyl having 1 to 6 carbon atoms, or alkoxy having 1 to 6 carbon atoms; A represents alkylene, carbonyl, imino, sulfide or disulfide. The alkyl represented by R^{11} to R^{17} and alkoxy represented by R^{13} to R^{15} may have about 1 to 6 carbon atoms. The cycloalkyl represented by R^{11} to R^{17} may have about 5 to 10 carbon atoms and the aryl represented by R^{11} to R^{15} and R^{17} may have about 6 to 10 carbon atoms. The alkylene represented by A may have about 1 to 6 carbon atoms and may be straight-chained or branched.

Among the basic compounds as described above, 2,6-dialkylpyridine compound represented by the formula (X) is preferable for improving the storage stability of the resist:



wherein R^{21} and R^{22} independently represent an alkyl having 1-4 carbon atoms. Concrete examples of the 2,6-dialkylpyridine compound include 2,6-lutidine, 2-ethyl-6-methylpyridine, 2,6-di-tert-butylpyridine, and the like. The

2,6-dialkylpyridine compound can be used alone or together with other basic compounds as a quencher.

The resist composition of the present invention preferably contains the resin in an amount in the range of 80
5 to 99.9 % by weight, and the acid generator in an of 0.1 to 20 % by weight based on the total amount of the resin and the acid generator.

In the resist composition of the present invention, the ratio by weight of the aliphatic sulfonium salt of the formula
10 (I) to the onium salt selected from the group consisting of a triphenylsulfonium salt of the formula (IIa) and a diphenyliodonium salt of the formula (IIb) is preferably about 9:1 to 1:9, more preferably about 8:2 to 2:8.

When a basic compound is used as a quencher, it is
15 preferably contained in an amount in the range of 0.0001 to 0.1 % by weight based on the total solid component weight of the resist composition. The composition may also contain, if required, various additives such as sensitizers, dissolution inhibitors, resins other than resin, surfactants, stabilizers,
20 and dyes so far as the objects of the present invention is not harmed.

The resist composition of the present invention generally becomes a resist solution in the state in which the above-described components are dissolved in a solvent to be
25 applied on a substrate such as a silicon wafer. The solvent herein used may be one which dissolves each component, has an appropriate drying rate, and provides a uniform and smooth coating after evaporation of the solvent, and can be one which

is generally used in this field. Examples thereof include glycol ether esters such as ethylcellosolve acetate, methylcellosolve acetate, and propylene glycol monomethyl ether acetate; esters such as ethyl lactate, butyl acetate, amyl acetate, and ethyl pyruvate; ketones such as acetone, methyl isobutyl ketone, 2-heptanone, and cyclohexanone; and cyclic esters such as γ -butyrolactone. These solvents can be used alone or in combination of two or more thereof.

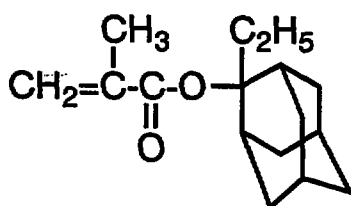
The resist film applied on a substrate, and dried is subjected to an exposure treatment for patterning. Then, after a heat-treatment for promoting a protecting deblocking reaction, development by an alkali developer is conducted. The alkali developer herein used can be various kinds of alkaline aqueous solutions used in this field. In general, an aqueous solution of tetramethylammoniumhydroxide or (2-hydroxyethyl)trimethylammoniumhydroxide (so-called colline) is often used.

The present invention will be described in more detail by way of examples, which should not be construed as limiting the scope of the present invention. All % and parts in examples are by weight unless otherwise stated. The weight-average molecular weight is a value determined from gel permeation chromatography using polystyrene as a reference standard.

Monomer Synthesis Example 1 (Synthesis of 2-ethyl-2-adamantyl methacrylate)

50 g of diethyl ether was added to 31.1 g of 2-adamantanone to form a solution. Then, 200 ml of a diethyl ether solution

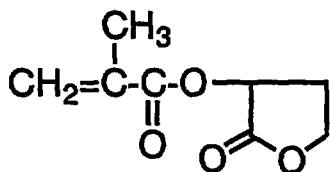
containing ethyl lithium in a concentration of 1.14 mole/liter was added dropwise thereto at such a rate as to keep the temperature of the solution not exceeding 10°C. After stirring the solution at 0°C for 2 hours as it was, 26.2 g of methacrylic acid chloride (1.2 mole times with respect to 2-methyl-2-adamantanol) was added dropwise thereto at such a rate as to keep the temperature of the solution not exceeding 10°C. After the completion of addition, the solution was stirred at room temperature for 12 hours. Thereafter, deposited inorganic salts were removed by filtration. The organic layer was washed with a 5% by weight aqueous solution of sodium bicarbonate and then washed twice with water. The organic layer was concentrated and distilled under reduced pressure to give 2-ethyl-2-adamantyl methacrylate represented by the following formula.



Monomer Synthesis Example 2 (Synthesis of α -methacryloyloxy- γ -butyrolactone)

100 g of α -bromo- γ -butyrolactone and 104.4 g of methacrylic acid (2.0 mole times with respect to α -bromo- γ -butyrolactone) were charged, and methyl isobutyl ketone was added thereto in an amount of three times the weight of α -bromo- γ -butyrolactone to form a solution. To this, 183.6

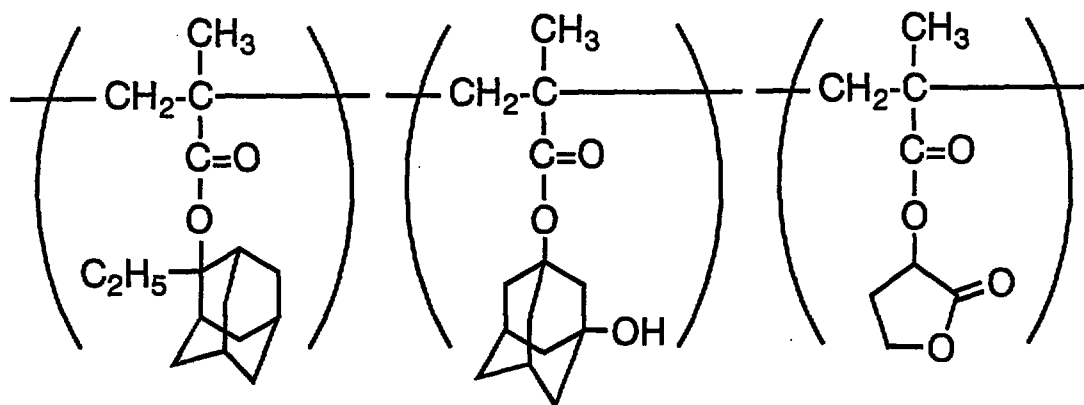
g of triethylamine (3.0 mole times with respect to
α-bromo-γ-butyrolactone) was added dropwise, followed by
stirring at room temperature for about 10 hours. After
filtration, an organic layer was washed with a 5% by weight
5 aqueous solution of sodium bicarbonate and then washed twice
with water. The organic layer was concentrated to give
α-methacryloyloxy-γ-butyrolactone represented by the following
formula.



10

Resin Synthesis Example (Synthesis of resin A)

2-Ethyl-2-adamantyl methacrylate,
3-hydroxy-1-adamantyl methacrylate and
α-methacryloyloxy-γ-butyrolactone were charged in a molar ratio
15 of 5 : 2.5 : 2.5 (20.0 g : 9.5 g : 7.3 g). Then, methyl isobutyl
ketone was added in two times by the weight of the total weight
of monomers to form a solution. As an initiator,
azobisisobutyronitrile was added in 2 mol% based on the total
amount of monomers, followed by heating at 80°C for about 8 hours.
20 Thereafter, the operation of pouring the reaction solution into
a large amount of heptane to cause precipitation was repeated
3 times, whereby purifying the product. As the result, a
copolymer having repeating units represented by the following
formula and having a weight average molecular weight of about
25 9,200 was obtained. The copolymer was referred to as resin A.

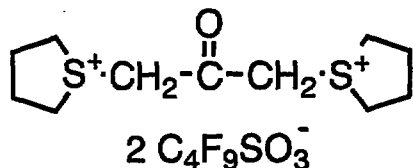


Synthesis Example 1 for Acid Generator: Synthesis of
1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiophenium)
bis(perfluorobutanesulfonate)

5 (1) Into a four-necked flask were charged 4.7 parts of tetrahydrothiophene, 5.2 parts of dibromoacetone and 47.1 parts of acetone, and they were stirred at room temperature for 24 hours. The deposited crystals were filtered and washed with acetone. The obtained filter cake was combined with ether and
10 the mixture was stirred. After filtration, the filter cake was washed with ether and dried to give 6.4 parts of 1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiophenium) dibromide. Yield: 66.9%.

(2) Into a four-necked flask were charged 1.5 part of
15 1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiophenium) dibromide obtained in (1) and 30 parts of acetonitrile. While stirring at room temperature, 2.6 parts of potassium perfluorobutanesulfonate was additionally charged. After stirring at room temperature for 24 hours, the mixture was
20 filtered to remove inorganic salts and the filtrate was concentrated. Thereto, butyl acetate was charged and the

mixture was stirred. After filtration, the filter cake was washed with ether and dried to give 1.8 part of the desired product. Yield: 57.2%.



¹H-NMR (DMSO-d₆, internal standard: tetramethylsilane), δ
5 (ppm): 2.17 - 2.23 (m, 8H), 3.46 - 3.59 (m, 8H), 4.67 (s, 4H)

Synthesis Example 2 for Acid Generator: Synthesis of
4-methyldiphenylsulfonium perfluorooctanesulfonate

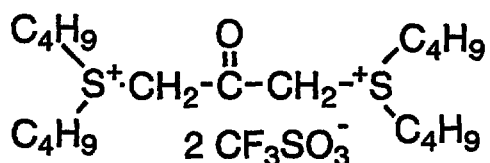
Into a four-necked flask were charged 8.0 parts of
10 diphenylsulfoxide and 80.0 parts of toluene, and the mixture
was cooled to 2°C. Then, 16.6 parts of trifluoroacetic anhydride
and 19.8 parts of perfluorooctanesulfonic acid were charged
and the mixture was stirred at the same temperature for 30 minutes.
After standing, a lower layer was concentrated and diluted with
15 340 parts of chloroform. The obtained chloroform solution was
washed 6 times with 85 parts of ion-exchange water and
concentrated to give 27.7 parts of the 4-methyldiphenylsulfonium
perfluorooctanesulfonate.

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20 Synthesis Example 3 for Acid Generator: Synthesis of
(2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
bis(trifluoromethanesulfonate)

Into a four-necked flask were charged 5.4 parts of dibutyl
sulfide, 5.2 parts of dibromoacetone and 54.5 parts of
25 acetonitrile. After stirring at room temperature for 2 hours,

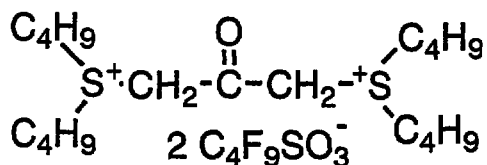
8.8 parts of silver trifluoromethanesulfonate was charged. After stirring at room temperature for 24 hours, the mixture was filtered to remove inorganic salts and the filtrate was concentrated. Thereto, butyl acetate was charged and the mixture was stirred. After filtration, the filter cake was washed with ether and dried to give 5.5 parts of the desired product. Yield: 49.9%.



¹H-NMR (CDCl₃, internal standard: tetramethylsilane), δ (ppm):
 0.97 - 1.02 (t, 12H), 1.46 - 1.60 (m, 8H), 1.75 - 1.86 (m, 8H),
 3.28 - 3.51 (m, 8H), 5.06 (s, 4H)

Synthesis Example 4 for Acid Generator: Synthesis of
 (2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
 bis(perfluorobutanesulfonate)

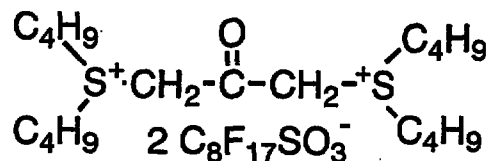
Into a four-necked flask were charged 4.4 parts of dibutyl sulfide, 4.3 parts of dibromoacetone and 44.4 parts of acetonitrile. After stirring at room temperature for 2 hours, 11.3 parts of silver perfluorobutanesulfonate was charged. After stirring at room temperature for 24 hours, the mixture was filtered to remove inorganic salts and the filtrate was concentrated. Thereto, butyl acetate was charged and the mixture was stirred. After filtration, the filter cake was washed with ether and dried to give 2.6 parts of the desired product. Yield: 17.7%.



¹H-NMR (CDCl₃, internal standard: tetramethylsilane), δ (ppm):
 0.97 - 1.02 (t, 12H), 1.46 - 1.60 (m, 8H), 1.74 - 1.86 (m, 8H),
 3.24 - 3.48 (m, 8H), 5.09 (s, 4H)

5 Synthesis Example 5 for Acid Generator: Synthesis of
 (2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
 bis(perfluorooctanesulfonate)

 Into a four-necked flask were charged 3.7 parts of dibutyl
 sulfide, 3.6 parts of dibromoacetone and 37.3 parts of
 10 acetonitrile. After stirring at room temperature for 2 hours,
 14.2 parts of silver perfluorooctanesulfonate was charged.
 After stirring at room temperature for 24 hours, the mixture
 was filtered to remove inorganic salts and the filtrate was
 concentrated. Thereto, butyl acetate was charged and the
 15 mixture was stirred. After filtration, the filter cake was
 washed with ether and dried to give 3.0 parts of the desired
 product. Yield: 17.2%.



¹H-NMR (CDCl₃, internal standard: tetramethylsilane), δ (ppm):
 0.96 - 1.01 (t, 12H), 1.45 - 1.58 (m, 8H), 1.73 - 1.85 (m, 8H),
 20 3.25 - 3.48 (m, 8H), 5.08 (s, 4H)

 Examples, described below, show preparation of resist

compositions with acid generators B to F, shown below, and evaluation.

Acid Generator B:

1,1'-(2-oxo-1,3-propanediyl)bis(tetrahydrothiophenium)
5 bis(perfluorobutanesulfonate) (the product in Synthesis
Example 1 for Acid Generator)

Acid Generator C: 4-methyldiphenylsulfonium
perfluorooctanesulfonate (the product in Synthesis Example 2
for Acid Generator)

10 Acid Generator D:

(2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
bis(trifluoromethanesulfonate) (the product in Synthesis
Example 3 for Acid Generator)

Acid Generator E:

15 (2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
bis(perfluorobutanesulfonate) (the product in Synthesis
Example 4 for Acid Generator)

Acid Generator F:

(2-oxo-1,3-propanediyl)bis(dibutylsulfonium)
20 bis(perfluorooctanesulfonate) (the product in Synthesis
Example 5 for Acid Generator)

Example 1

Components listed below were mixed and dissolved. The
25 resultant solution was filtered through a fluorine resin filter
having a pore diameter of 0.2 μm to give a resist solution.

Resin A

10 parts

Acid generator B	0.25 part
Acid generator C	0.2 part
Quencher: 2,6-diisopropylaniline	0.02 part
2,6-litidine	0.01 part
5 Solvent: propyleneglycol monomethylether acetate	
	60.8 parts
γ -butyrolactone	3.2 parts

On a silicon wafer, a composition "DUV-30J-14"

10 manufactured by Brewer Co. Ltd. was applied and baked under conditions of 215°C for 60 seconds so that an organic anti-reflective layer having a thickness of 1,600 angstrom was formed on the wafer. The resist solution obtained above was applied by spin-coating on said wafer so that the film thickness

15 after drying was 0.335 μm . After applying the resist solution, the wafer was pre-baked on a direct hotplate at 120°C for 60 seconds.

The wafer having a resist film formed thereon was irradiated with an ArF eximer stepper ["NSR-ArF", manufactured

20 by Nikon, NA = 0.55, σ = 0.6] through a line-and-space pattern, changing stepwise the exposure amount. The exposed wafer was subjected to post-exposure baking (PEB) on a hot plate at 150°C for 60 seconds. Then the wafer was subjected to paddle development with 2.38% by weight aqueous tetramethyl ammonium

25 hydroxide solution for 60 seconds. The developed pattern was observed by a scanning electron microscope and assessed for the effective sensitivity and the resolution by the following methods. The effective sensitivity was 88mJ/cm², and the

resolution was 0.13 μm .

Effective sensitivity: This is expressed in the minimum amount of exposure which gave 1 : 1 line-and-space pattern of 0.18 μm .

5 Resolution : This is expressed in the minimum size which gave line-and-space pattern spitted at the exposure amount of the effective sensitivity.

Cross sectional photograph by a scanning electron microscope of Line-and-space pattern of 0.18 μm at exposure
10 amount of the effective sensitivity was observed. It was observed that sides of the pattern were vertical and the top surfaces of the pattern were almost flat.

The above resist solutions were applied on quartz glass
15 wafers to form resist films having a film thickness after prebake of 0.355 μm . The transmittance of resist films at 193 nm was measured with a spectrophotometer. As the result, a transmittance of 67% was obtained. As described above, these resists showed a high transmittance and had a good resolution.

20

Examples 2-4 and Comparative Example 1

Components listed below were mixed and dissolved. The resultant solution was filtered through a fluorine resin filter having a pore diameter of 0.2 μm to give a resist solution.

25

Resin A	10 parts
Acid generator (1) shown in Table 1	0.5 part
Acid generator C	0.2 part

Quencher: 2,6-diisopropylaniline	0.015 part
Solvent: propyleneglycol monomethylether acetate	60.8 parts
γ -butyrolactone	3.2 parts

5

On a silicon wafer, a composition "DUV-30J-14" manufactured by Brewer Co. Ltd. was applied and baked under conditions of 215°C for 60 seconds so that an organic anti-reflective layer having a thickness of 1,600 angstrom was formed on the wafer. The resist solution obtained above was applied by spin-coating on said wafer so that the film thickness after drying was 0.335 μm . After applying the resist solution, the wafer was pre-baked on a direct hotplate at 110°C for 60 seconds.

15

The wafer having a resist film formed thereon was irradiated with an ArF excimer stepper ["NSR-ArF", manufactured by Nikon, NA = 0.55, σ = 0.6] through a line-and-space pattern, changing stepwise the exposure amount. The exposed wafer was subjected to post-exposure baking (PEB) on a hot plate at 150°C for 60 seconds. Then the wafer was subjected to paddle development with 2.38% by weight aqueous tetramethyl ammonium hydroxide solution for 60 seconds. The developed pattern was observed by a scanning electron microscope and assessed for the effective sensitivity and the resolution by the methods above. The results are shown in Table 1.

20

25

The above resist solutions were applied on quartz glass wafers to form resist films having a film thickness after prebake of 0.355 μm . The transmittance of resist films at 193 nm was

measured with a spectrophotometer. This result is also shown in Table 1.

Table 1

Example No.	Acid generator (1)	Effective sensitivity (mJ/cm ²)	Resolution (μm)	Transmittance (%)
Example 2	D	51	0.16	71
Example 3	E	57	0.15	67
Example 4	F	69	0.15	67
Comparative Example 1	none	59	0.17	71

5

The chemical amplification type positive resist composition of the invention, which contains specific acid generators, has high transmittance, is superior in sensitivity and resolution in a lithography utilizing a light having a wavelength of 220 nm or lower, for example, ArF excimer laser light, and confers a good profile.

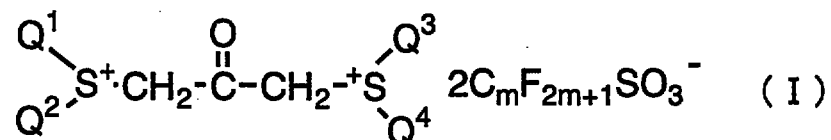
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What is claimed is:

1. A chemical amplifying type positive resist composition comprising

an aliphatic sulfonium salt represented by the following formula

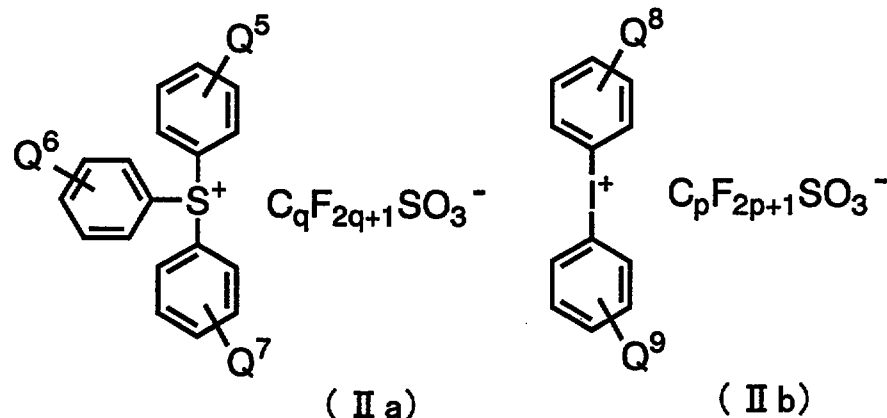
5 (I):



wherein either Q^1 , Q^2 , Q^3 and Q^4 independently represent an alkyl group having 1 to 6 carbon atoms or a cycloalkyl group having 3 to 10 carbon atoms, or Q^1 and Q^2 and/or Q^3 and Q^4 independently form, together with the adjacent sulfur atom, a heterocyclic group which has 2 to 8 carbon atoms and which may further have an oxygen atom or a sulfur atom, and m represents an integer of 1 to 8;

at least one onium salt selected from the group consisting of a triphenylsulfonium salt represented by the following formula

15 (IIa) and a diphenyliodonium salt represented by the following formula (IIb):



wherein Q^5 , Q^6 , Q^7 , Q^8 and Q^9 independently represent a hydrogen atom, a hydroxyl group, an alkyl group having 1 to 6 carbon



atoms or an alkoxy group having 1 to 6 carbon atoms, and p and q represent integer of 1 to 8; and

a resin which contains a polymerization unit having a group unstable to an acid, and which is insoluble in alkali by itself
5 but becomes soluble in alkali by the action of an acid.

2. The chemical amplifying type positive resist composition according to claim 1 wherein the ratio by weight of the aliphatic sulfonium salt of the formula (I) to the onium salt selected from the group consisting of a triphenylsulfonium salt of the
10 formula (IIa) and a diphenyliodonium salt of the formula (IIb) is about 9:1 to 1:9

3. The chemical amplifying type positive resist composition according to claim 1 wherein the resin contains the polymerization unit having a group unstable to an acid in a
15 range of 10 to 80% by mole based on the total resin.

4. The chemical amplifying type positive resist composition according to claim 1 wherein the polymerization unit having a group unstable to an acid is a polymerization unit of 2-alkyl-2-adamantyl (meth)acrylate.

20 5. The chemical amplifying type positive resist composition according to claim 1 wherein the resin further contain a polymerization unit selected from polymerization units of 3-hydroxy-1-adamantyl (meth)acrylate and polymerization units of (meth)acryloyloxy- γ -butyrolactone in which the lactone ring
25 is unsubstituted or substituted with an alkyl.

6. The chemical amplifying type positive resist composition according to claim 5 wherein the resin is a terpolymer containing a polymerization unit having a group unstable to an acid, a



polymerization unit of 3-hydroxy-1-adamantyl (meth)acrylate and a polymerization unit of (meth)acryloyloxy- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl.

5 7. The chemical amplifying type positive resist composition according to claim 5 wherein the polymerization unit of (meth)acryloyloxy- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl is a polymerization unit of α -(meth)acryloyloxy- γ -butyrolactone which is
10 unsubstituted or alkyl-substituted in the lactone ring, or a polymerization unit of β -(meth)acryloyloxy- γ -butyrolactone which is unsubstituted or alkyl-substituted in the lactone ring.

8. The chemical amplifying type positive resist composition according to claim 1 wherein the resin further contains a
15 polymerization unit of aliphatic unsaturated dicarboxylic anhydride and a polymerization unit of 2-norbornene.

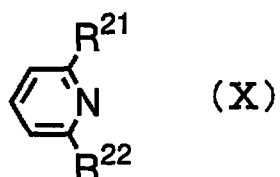
9. The chemical amplifying type positive resist composition according to claim 8 wherein the resin is a polymer containing a polymerization unit of aliphatic unsaturated dicarboxylic
20 anhydride and a polymerization unit of 2-norbornene as well as a polymerization unit selected from a polymerization units of 3-hydroxy-1-adamantyl (meth)acrylate and polymerization units of (meth)acryloyloxy- γ -butyrolactone in which the lactone ring is unsubstituted or substituted with an alkyl.

25 10. The chemical amplifying type positive resist composition according to claim 1 which further comprises a basic compound as a quencher.

11. The chemical amplifying type positive resist composition

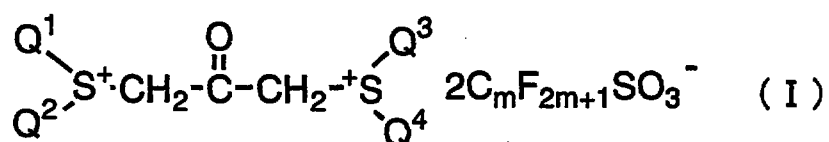


according to claim 10 wherein the basic compound is 2,6-dialkylpyridine compound represented by the formula (X):



wherein R^{21} and R^{22} independently represent an alkyl having 1-4 carbon atoms.

- 5 12. An aliphatic sulfonium salt represented by the following formula (I):



- wherein either Q^1 , Q^2 , Q^3 and Q^4 independently represent an alkyl group having 1 to 6 carbon atoms or a cycloalkyl group having 3 to 10 carbon atoms, or Q^1 and Q^2 and/or Q^3 and Q^4 independently form, together with the adjacent sulfur atom, a heterocyclic group which has 2 to 8 carbon atoms and which may further have an oxygen atom or a sulfur atom, and m represents an integer of 1 to 8
- 10

