

ADDITIVE FOR RESIST AND RESIST COMPOSITION COMPRISING SAME

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to a resist additive which improves hydrophobicity of the surface of a resist film to prevent materials from being leached from the resist film in water during an immersion lithography process and forms a micropattern of the resist film with
10 excellent sensitivity and high resolution, and a resist composition including the same.

Description of the Related Art

 With higher integration and higher speed of large
15 scale integrated circuits (LSI) in recent years, accurate micropatterning of photoresist is required. As exposure light sources used in the formation of resist patterns, a g-line (436 nm) or i-line (365 nm) from a mercury lamp has been widely used.

20 However, as resolution improvement obtained by adjusting exposure wavelength approaches physical limits, a method of using shorter wavelength was introduced as a finer patterning technology of a photoresist. For example, a KrF excimer laser (248 nm), an ArF excimer laser, or the like
25 having a shorter wavelength than i-line (365 nm) is being

used.

In ArF immersion lithography using an ArF excimer laser as a light source, the space between a projection lens and a wafer substrate is filled with water. According to this method, a pattern may be formed using a refractive index of water at 193 nm even when a lens having an NA of 1.0 or greater is used, and this method is commonly referred to as immersion lithography. However, since a resist film directly contacts water, acids generated by a photoacid generator or amine compounds contained in the resist film as a quencher may be easily dissolved in water. Thus, the resist pattern may be deformed or may collapse due to swelling, or various defects such as bubbles and watermarks may be generated.

Accordingly, a method of forming a protective film or an upper film between the resist film and water to prevent the resist film from coming in contact with a medium such as water has been introduced. Such resist protective films need to be formed on a resist film while having sufficient light transmittance at the exposure wavelength so as not to interrupt exposure without being intermixed with the resist film, need to have and maintain stability without being leached by a medium such as water during liquid immersion lithography, and need to be easily dissolved in an alkali solution that is a developer during development.

Prior Art

Patent Document 1: Korean Patent Application
Publication No. 2006-0029280 (published on April 5, 2006)

Patent Document 2: Korean Patent Application
5 Publication No. 2009-0108935 (published on October 19, 2009)

Patent Document 3: Korean Patent Application
Publication No. 2011-0084848 (published on July 26, 2011)

SUMMARY OF THE INVENTION

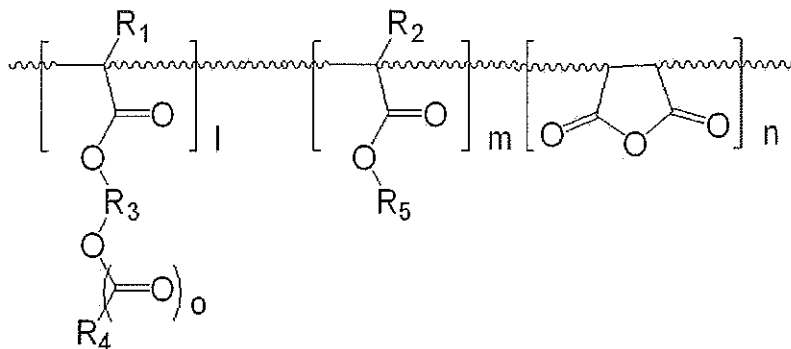
10 Therefore, the present invention has been made in
view of the above problems, and it is an object of the
present invention to provide a resist additive which
improves hydrophobicity of the surface of a resist film to
prevent materials from being leached from the resist film
15 in water during an immersion lithography process. While
the resist additive is dissolved in a developer with a
resist at exposed regions, the resist additive remains
with the resist to form a pattern and is converted to have
hydrophilicity by the developer at non-exposed regions.

20 It is another object of the present invention to
provide a resist composition including the resist additive
and a method of forming a resist pattern using the
composition.

25 In accordance with the present invention, the above
and other objects can be accomplished by the provision of

a resist additive represented by Formula 1 below.

Formula 1

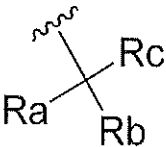
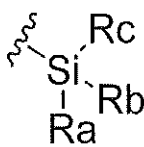
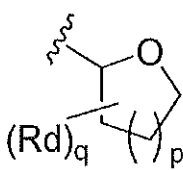


In Formula 1, R_1 and R_2 may be each independently a hydrogen atom or a C1-C8 alkyl group.

R_3 may be selected from the group consisting of a C1-C20 alkanediyl group, a C2-C20 alkenediyl group, a C1-C20 heteroalkanediyl group, a C2-C20 heteroalkenediyl group, a C3-C30 cycloalkanediyl group, a C3-C30 cycloalkenediyl group, a C2-C30 heterocycloalkanediyl group, and a C3-C30 heterocycloalkanediyl group in which at least one hydrogen atom is substituted with one group selected from the group consisting of a C1-C10 alkyl group, a C1-C20 haloalkyl group, and a C3-C30 cycloalkyl group or unsubstituted.

R_4 may be a hydrophobic group selected from the group consisting of a C1-C20 haloalkyl group, an organic silicon group, and a C3-C20 hydrocarbon group.

R_5 may be an acid labile group selected from the

group consisting of , , and .

Here, R_a , R_b , R_c and R_d may be each independently selected from the group consisting of a C1-C20 alkyl group, a C3-C30 cycloalkyl group, a (C1-C10 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C20 alkoxy group, a (C1-C10 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C1-C10 alkyl)carboxyl group, a (C3-C18 cycloalkyl)carboxyl group, and a C3-C30 heterocycloalkyl group, or fused together between adjacent groups to form a C3-C30 saturated or unsaturated hydrocarbon ring or a C2-C30 heterocyclic group, p may be an integer of 0 to 3, and q may be an integer of 0 to 10.

Here, l , m , and n are respectively numbers of the repeat units in a backbone, wherein $l+m+n=1$, $0 < l/(l+m+n) < 0.99$, $0 \leq m/(l+m+n) < 0.99$, and $0 < n/(l+m+n) \leq 0.20$.

Here, o is an integer of 0 or 1. If o is 0, R_4 is an organic silicon group, and if o is 1, R_4 is a C1-C20 haloalkyl group or a C3-C20 hydrocarbon group.

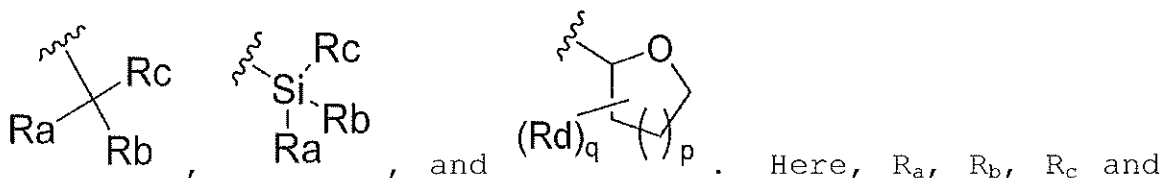
R_3 may be selected from the group consisting of a C1-C10 alkanediyl group, a C2-C10 alkenediyl group, a C1-C10 heteroalkanediyl group, a C2-C10 heteroalkenediyl group, a C3-C18 cycloalkanediyl group, a C3-C18 cycloalkenediyl group, a C2-C18 heterocycloalkanediyl group, and a C3-C18

heterocycloalkanediyl group in which at least one hydrogen atom is substituted with a C1-C10 alkyl group or a C1-C10 haloalkyl group or unsubstituted.

R_4 may be selected from the group consisting of a C1-C10 fluoroalkyl group, a silyl group, a C1-C10 alkylsilyl group, a C3-C10 linear or branched alkyl group, a C3-C14 monocyclic cycloalkyl group, a C8-C18 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl group, and a C10-C30 tetracyclic cycloalkyl group.

R_4 may be selected from the group consisting of a t-butyl group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl group, and a heptafluoropropyl group.

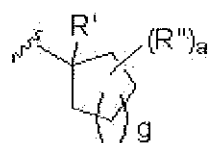
R_5 may be selected from the group consisting of



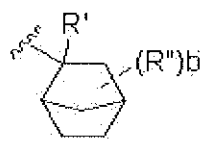
Rd may be each independently selected from the group consisting of a C1-C10 alkyl group, a C3-C14 monocyclic cycloalkyl group, a C8-C20 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl group, a C10-C30 tetracyclic cycloalkyl group, a (C1-C5 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C10 alkoxy group, a (C1-C5 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C1-C5 alkyl)carboxyl group, and a

(C3-C10 cycloalkyl)carboxyl group or fused together between adjacent groups to form a C6-C18 saturated or unsaturated hydrocarbon ring or a C5-C18 heterocyclic group, p may be an integer of 0 to 3, and q may be an integer of 0 to 5.

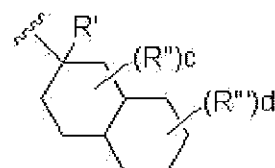
R₅ may be selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxy-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by Formulae 2a to 2k below.



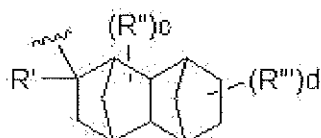
(2a)



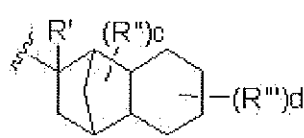
(2b)



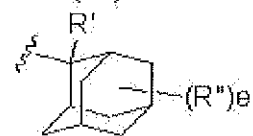
(2c)



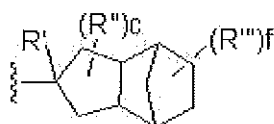
(2d)



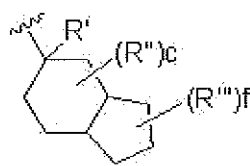
(2e)



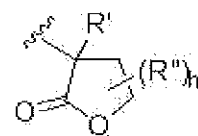
(2f)



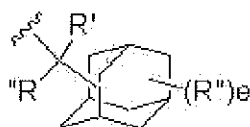
(2g)



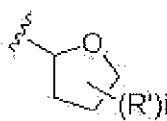
(2h)



(2i)



(2j)

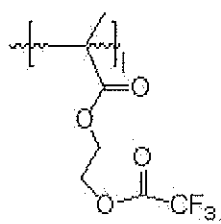


(2k)

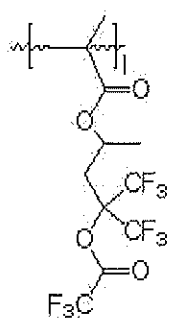
In Formulae 2a to 2k, R', R'' and R''' may be each independently a hydrogen atom or a C1-C10 alkyl group, a and e may be each independently an integer of 0 to 15, b may be an integer of 0 to 11, c and d may be each independently an integer of 0 to 9, f may be an integer of 0 to 7, g and i may be each independently an integer of 0 to 6, h may be an integer of 0 to 4, $0 \leq c+d \leq 17$, and $0 \leq c+f \leq 15$.

A repeat unit 1 may be selected from the group consisting of repeat units represented by Formulae 3a to

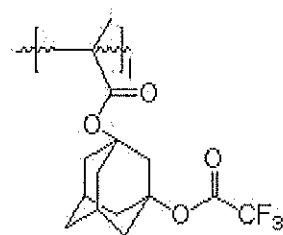
3i below.



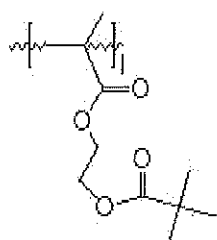
(3a)



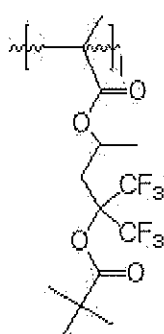
(3b)



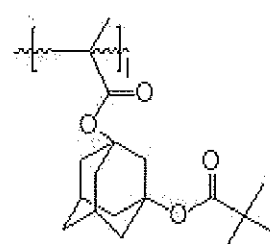
(3c)



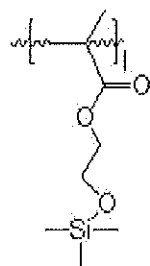
(3d)



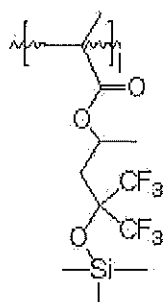
(3e)



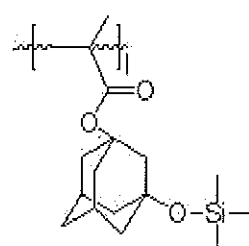
(3f)



(3g)

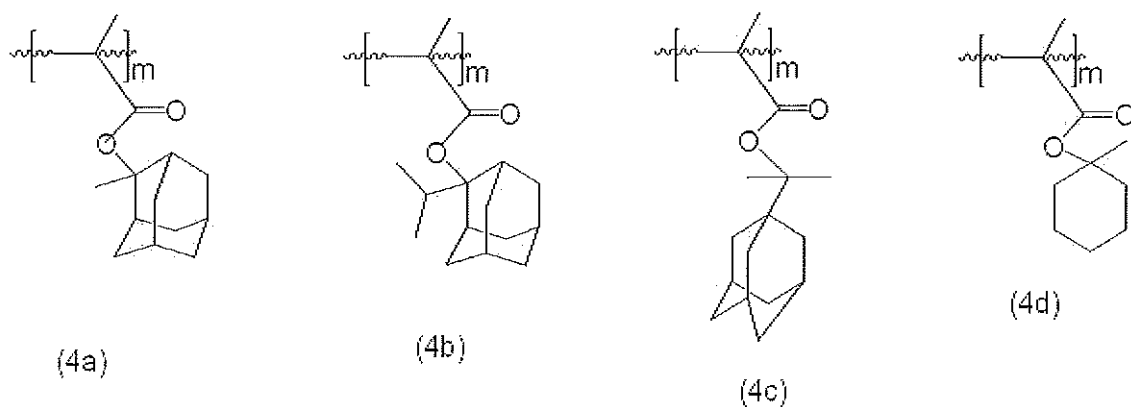


(3h)



(3i)

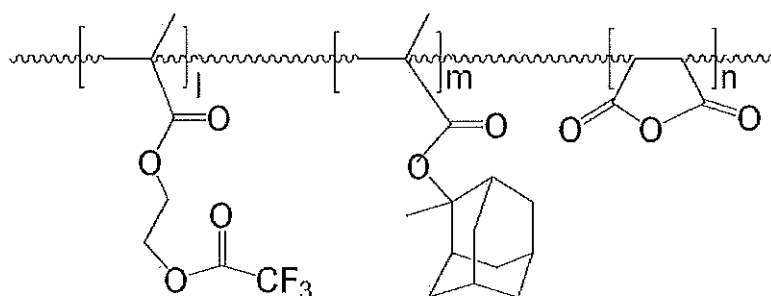
A repeat unit m may be selected from the group consisting of repeat units represented by Formulae 4a to 4d below.



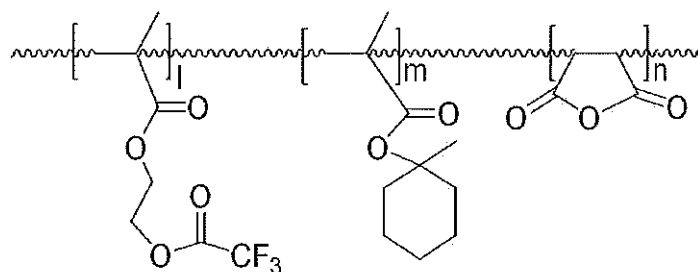
A repeat unit n of Formula 1 may be contained in a copolymer of the resist additive in an amount of 5 to 15 mol%.

5 The resist additive may be selected from the group consisting of compounds represented by Formulae 5 to 16 below.

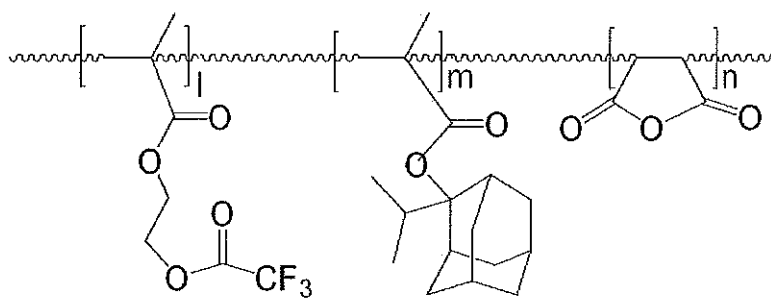
Formula 5



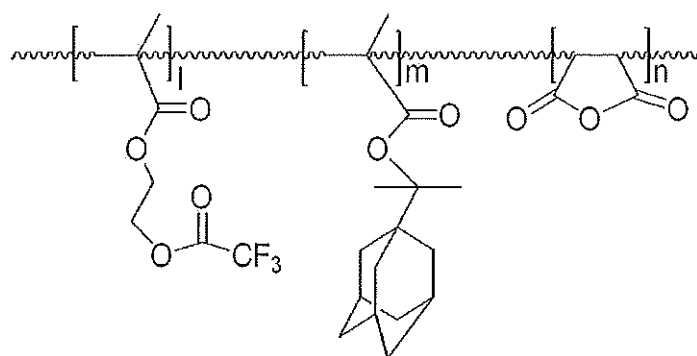
10 Formula 6



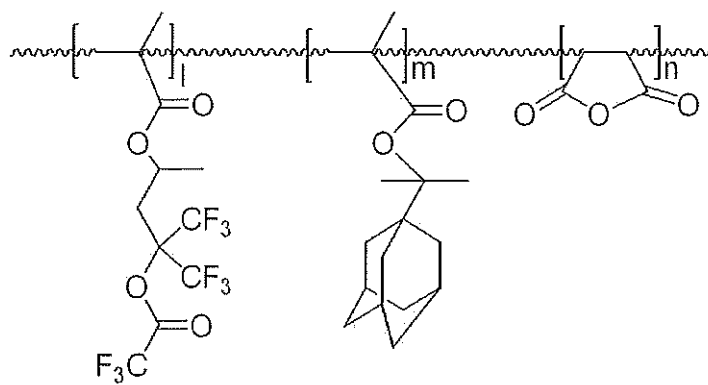
Formula 7



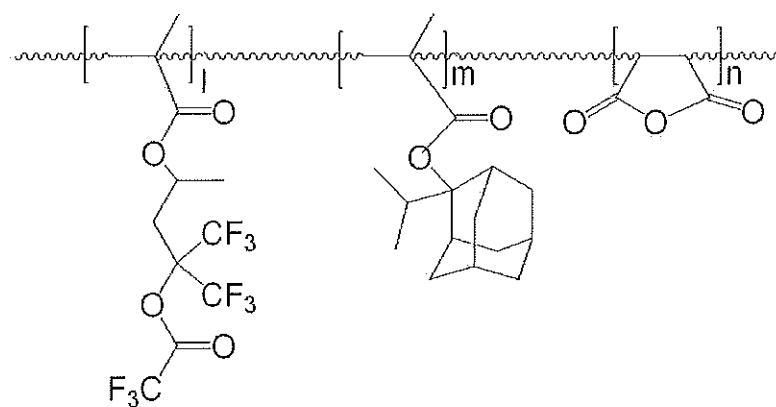
Formula 8



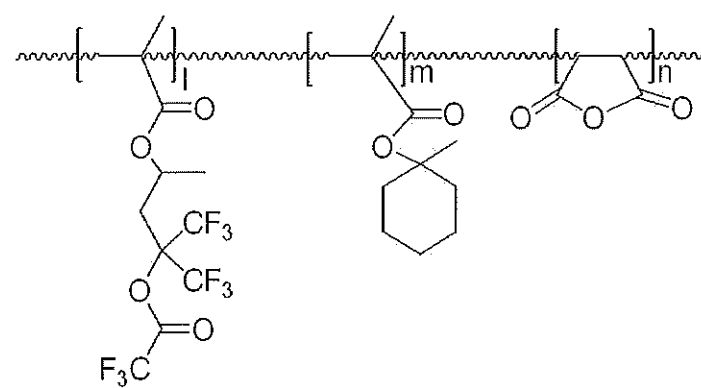
Formula 9



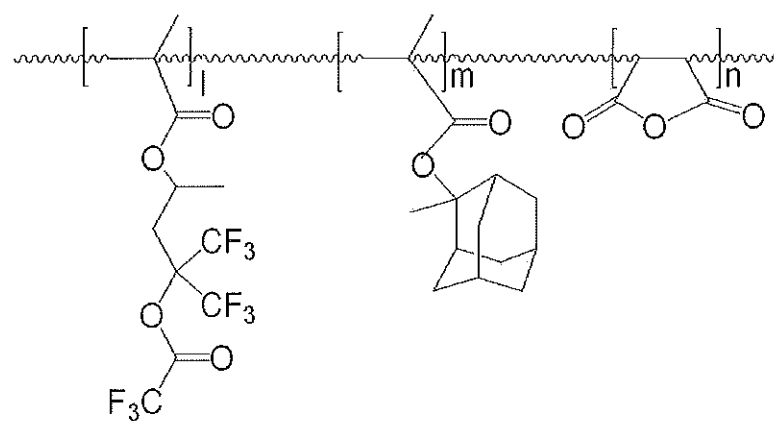
Formula 10



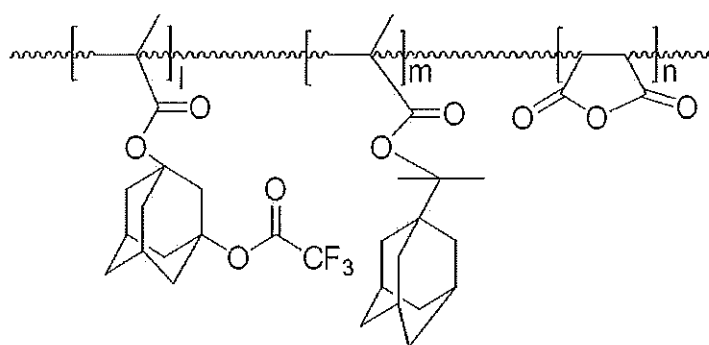
Formula 11



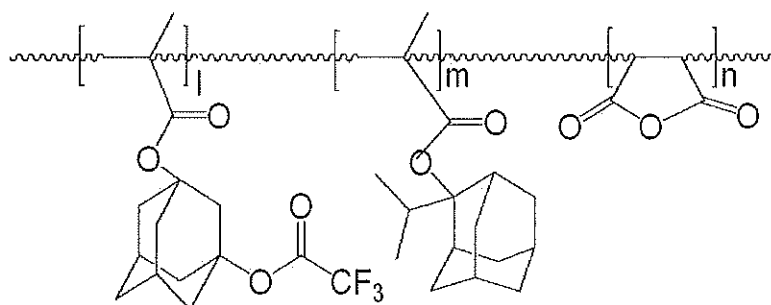
Formula 12



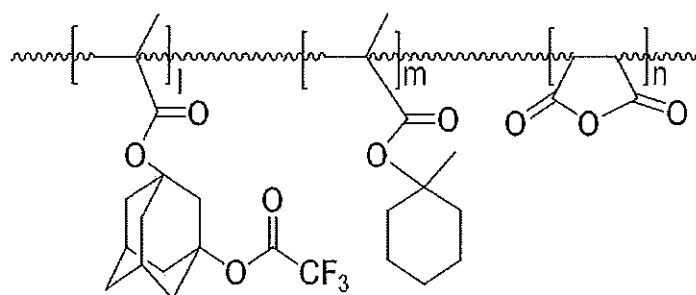
Formula 13



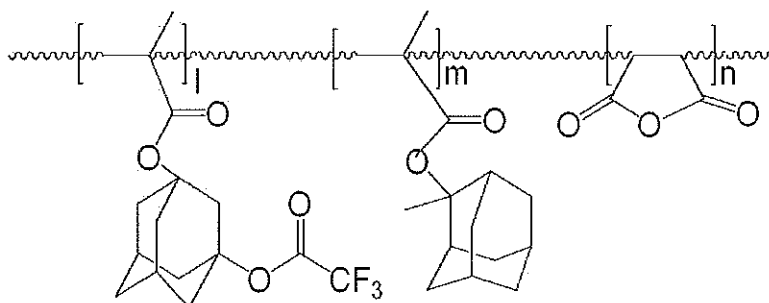
Formula 14



Formula 15



Formula 16



In Formulae 5 to 16, 1, m, and n are respectively numbers of the repeat units in a backbone, wherein

$l+m+n=1$, $0 < l/(l+m+n) < 0.99$, $0 \leq m/(l+m+n) < 0.99$, and
 $0 < n/(l+m+n) \leq 0.20$.

A polystyrene equivalent weight average molecular weight of the resist additive measured using gel permeation chromatography may be in the range of 1,000 to 500,000 g/mol.

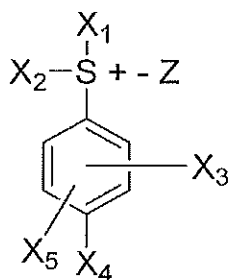
A weight average molecular weight/number average molecular weight ratio of the resist additive may be in the range of 1 to 5.

In accordance with an aspect of the present invention, the above and other objects can be accomplished by the provision of a resist composition including the resist additive, a resist base polymer, an acid generator, and a solvent.

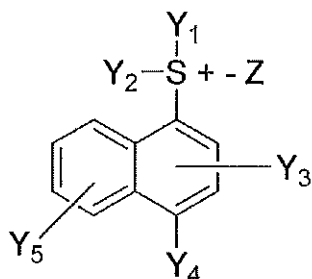
The amount of the resist additive may be in the range of 0.05 to 5% by weight based on the total weight of the resist composition.

The acid generator may include at least one compound selected from the group consisting of compounds represented by Formulae 20 and 21 below.

Formula 20



Formula 21

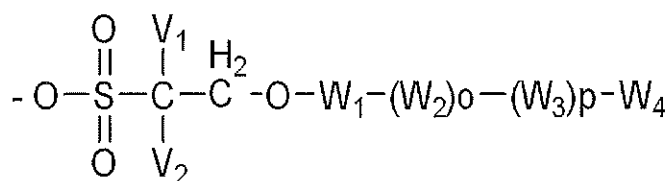


In Formulae 20 and 21, X_1 , X_2 , Y_1 , and Y_2 may be each
 5 independently selected from the group consisting of a
 hydrogen atom, a C1-C10 alkyl group, an allyl group, a
 perfluoroalkyl group, a benzyl group, a C6-C30 aryl group,
 and any combination thereof, wherein X_1 and X_2 are fused to
 form a C3-C30 saturated or unsaturated hydrocarbon ring,
 10 and Y_1 and Y_2 are fused to form a C3-C30 saturated or
 unsaturated hydrocarbon ring

X_3 , X_4 , X_5 , Y_3 , Y_4 , and Y_5 may be each independently
 selected from the group consisting of a hydrogen atom, a
 C1-C30 alkyl group, a halogen group, a C1-C30 alkoxy
 15 group, a C6-C30 aryl group, a thiophenoxy group, a C1-C30
 thioalkoxy group, a C1-C20 alkoxy carbonyl methoxy group,
 and any combination thereof.

Z, which denotes an anion, may be OSO_2CF_3 , $\text{OSO}_2\text{C}_4\text{F}_9$, $\text{OSO}_2\text{C}_8\text{F}_{17}$, $\text{N}(\text{CF}_3)_2$, $\text{N}(\text{C}_2\text{F}_5)_2$, $\text{N}(\text{C}_4\text{F}_9)_2$, $\text{C}(\text{CF}_3)_3$, $\text{C}(\text{C}_2\text{F}_5)_3$, $\text{C}(\text{C}_4\text{F}_9)_3$, or a functional group represented by Formula 22 below.

Formula 22



5

In Formula 22, V_1 and V_2 may be each independently a halogen atom,

W_1 may be $-(\text{C}=\text{O})-$ or $-(\text{SO}_2)-$.

W_2 may be a C1-C10 alkanediyl group.

10 W_3 may be selected from the group consisting of a C3-C30 cycloalkyl group, a C6-C30 aryl group, a C7-C30 aralkyl group, a C6-C30 aryloxy group, a C6-C30 arylthio group, and a C5-C30 heterocyclic group.

15 W_4 may be selected from the group consisting of a hydrogen atom, a halogen group, a C1-C10 alkyl group, a C1-C10 alkoxy group, a C1-C10 haloalkyl group, a C1-C10 alkylthio group, a C6-C30 aryl group, and any combination thereof.

20 Here, o is an integer of 0 to 1, and p is an integer of 0 to 2.

The amount of the acid generator may be in the range of 0.3 to 10 parts by weight based on 100 parts by weight of solids of the resist composition.

The resist composition may further include an additive selected from the group consisting of an alkali soluble quencher, an acid diffusion quencher, a surfactant, and any mixture thereof.

5 In accordance with another aspect of the present invention, there is provided a method of forming a resist pattern including forming a resist film by coating the resist composition on a substrate, heating the resist film, and exposing the resist film to light to form a
10 predetermined pattern, and developing the exposed pattern.

The exposing may be performed using a light source selected from the group consisting of a KrF excimer laser, an ArF excimer laser, an extreme ultraviolet laser, an X-ray, and an electron beam.

15 Other aspects, features, and advantages of the present invention will be more clearly understood from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

20 Hereinafter, the present invention will be described in detail. The following detailed description

of the present invention is intended to provide further explanation of the invention as claimed.

The terms 'halo' or 'halogen atom' as used herein refers to fluorine, chlorine, bromine, or iodine atoms, unless otherwise stated.

The term 'hetero' as used herein is intended to encompass 1 to 3 hetero atoms selected from the group consisting of N, O, S, and P substituting for carbon atoms, unless otherwise stated. For example, the term "heteroalkyl group" refers to an alkyl group in which 1 to 3 carbon atoms are replaced by the hetero atoms.

The term 'alkyl group' as used herein refers to a linear or branched C1-C30 alkyl group, unless otherwise stated, and the alkyl group includes a primary alkyl group, a secondary alkyl group, and a tertiary alkyl group. Examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, and a t-butyl group, but are not limited thereto.

The term 'cycloalkyl group' as used herein refers to a C3-C30 cycloalkyl group, unless otherwise stated, and includes monocyclic, dicyclic, tricyclic, and tetracyclic alkyl groups. The cycloalkyl also includes an adamantyl group, a norbornyl group, and a polycyclic cycloalkyl group including a norbornyl group.

The term 'alkanediyl group' as used herein refers to a divalent atomic group derived from alkanes by removal of two hydrogen atoms and may be represented by the general formula $-C_nH_{2n}-$. The term 'alkenediyl group' as used herein refers to a divalent atomic group derived from alkenes by removal of two hydrogen atoms and may be represented by the general formula $-C_nH_n-$.

The term 'aryl group' as used herein refers to a group including a benzene ring and derivatives thereof, unless otherwise stated. For example, the aryl group includes toluene or xylene consisting of a benzene ring with an alkyl side chain, biphenyl consisting of at least two benzene rings connected via a single bond, fluorene, xanthene or anthraquinone consisting of at least two benzene rings connected via a cycloalkyl group or heterocycloalkyl group, and naphthalene or anthracene consisting of at least two benzene rings condensed to each other. Unless otherwise stated herein, the aryl group refers to a C6-C30 aryl group.

The term 'hydrocarbon group' as used herein refers to a C3-C20 monovalent hydrocarbon group consisting of carbon and hydrogen, unless otherwise stated, and may include an aliphatic linear or branched hydrocarbon group and an alicyclic hydrocarbon group. Examples of the hydrocarbon group include a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl

group, a cyclohexyl group, a phenyl group, a tolyl group, a xylyl group, a mesityl group, a benzyl group, a diphenylmethyl group, a triphenylmethyl group, a styryl group, a biphenyl group, and a naphthyl group.

5 The term 'heterocycle' as used herein refers to a cyclic radical having 4 to 20 ring atoms derived by substituting one or more, e.g., 1, 2, 3 or 4, carbon atoms with hetero atoms, e.g., N, O, P or S, unless otherwise stated. The heterocycle includes a saturated ring, a
10 partially unsaturated ring, and an aromatic ring, i.e., a heteroaromatic ring having heteroatoms oxidized or quarternized to form, for example, N-oxides or quaternary salts. Substituted heterocycles include a carbonyl group and a heterocyclic ring substituted with any substituent
15 disclosed herein.

 Examples of the heterocycles include pyridyl, dihydropyridyl, tetrahydropyridyl(piperidyl), thiazolyl, tetrahydrothiophenyl, sulfur oxidized tetrahydrothiophenyl, pyrimidinyl, furanyl, thienyl, pyrrolyl, pyrazolyl,
20 imidazolyl, tetrazolyl, benzofuranyl, thianaphthalenyl, indolyl, indolenyl, quinolinyl, isoquinolinyl, benzimidazolyl, piperidinyl, 4-piperidonyl, pyrrolidinyl, 2-pyrrolidonyl, pyrrolinyl, tetrahydrofuranyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl,
25 decahydroquinolinyl, octahydroisoquinolinyl, azocinyl,

triazinyl, 6H-1,2,5-thiadiazinyl, 2H,6H-1,5,2-dithiazinyl,
thienyl, thianthrenyl, pyranyl, isobenzofuranyl, chromenyl,
xanthenyl, phenoxathinyl, 2H-pyrrolyl, isothiazolyl,
isoxazolyl, pyrazinyl, pyridazinyl, indolizinyl, isoindolyl,
5 3H-indolyl, 1H-indazolyl, purinyl, 4H-quinolizinyl,
phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl,
cinnolinyl, pteridinyl, 4aH-carbazolyl, carbazolyl, β -
carbolinyl, phenanthridinyl, acridinyl, pirimidinyl,
phenanthrolinyl, phenazinyl, phenothiazinyl, furazanyl,
10 phenoxazinyl, isochromanlyl, chromanlyl, imidazolidinyl,
imidazolinyl, pyrazolidinyl, pyrazolinyl, piperazinyl,
indolinyl, isoindolinyl, quinuclidinyl, morpholinyl,
oxazolidinyl, benzotriazolyl, benzisoxazolyl, oxindolyl,
benzoxazolinyl, isatinoyl, and bis-tetrahydrofuranyl, which
15 may be substituted or unsubstituted, N-oxides thereof (for
example, pyridyl N-oxide and quinolinyl N-oxide) or
quaternary salts thereof, but are not limited thereto.

All compounds or substituents used herein may be
substituted or unsubstituted, unless stated otherwise. In
20 this regard, the term 'substituted' indicates that hydrogen
is substituted with one selected from the group consisting
of a halogen atom, a hydroxyl group, a carboxyl group, a
cyano group, a nitro group, an amino group, a thio group, a
methylthio group, an alkoxy group, a nitrile group, an
25 aldehyde group, an epoxy group, an ether group, an ester

group, a carbonyl group, an acetal group, a ketone group, an alkyl group, a perfluoroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an allyl group, a benzyl group, an aryl group, a heteroaryl group, any derivative thereof, and
5 any combination thereof.

The term 'combination thereof' as used herein refers to at least two substituents bound to each other by a single bond or a linking group, or at least two substituents condensed to each other, unless stated otherwise.

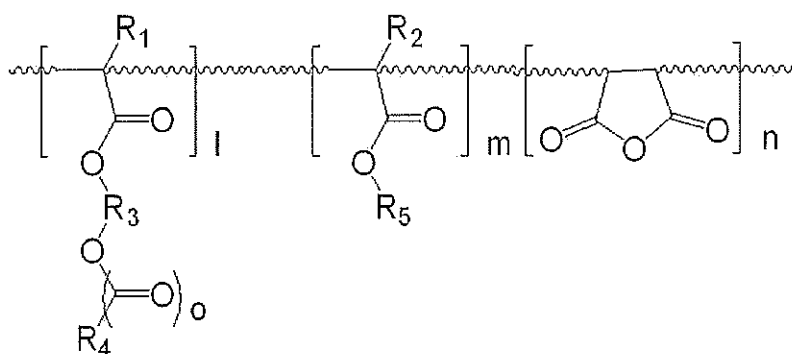
10 Conventionally, when a resist pattern is formed by ArF immersion lithography, water is used in a light path on a photoresist film in order to increase refractive index. However, acids or amine compounds contained in a resist film are dissolved in water disposed between a projection lens
15 and a wafer substrate, and accordingly the projection lens may be contaminated, the resist pattern may be deformed or collapse due to swelling, or various defects such as bubbles and watermarks may be generated.

According to the present invention, a copolymer for an
20 additive functioning as a protective film for a resist film and convertible to have hydrophilicity is provided. An acrylic acid-derived repeat unit and a maleic anhydride-derived repeat unit contained in the backbone of the copolymer form carboxyl groups by a developer at non-exposed
25 regions such that hydrophilicity of the surface of the

resist film is improved, thereby inhibiting defects of the copolymer. A hydrophobic group contained at one end of a side chain of the copolymer improves hydrophobicity of the surface of the resist film during exposure to prevent materials from being leached from the resist film during immersion lithography and is converted to a hydrophilic group during development to provide hydrophilicity to the copolymer.

That is, a copolymer according to an embodiment of the present invention is a multiblock copolymer represented by Formula 1 below.

Formula 1



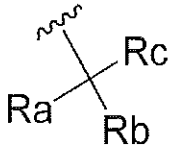
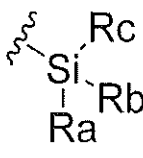
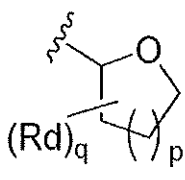
In Formula 1, R_1 and R_2 may be each independently a hydrogen atom or a C1-C8 alkyl group.

R_3 may be selected from the group consisting of a C1-C20 alkanediyl group, a C2-C20 alkenediyl group, a C1-C20 heteroalkanediyl group, a C2-C20 heteroalkenediyl group, a C3-C30 cycloalkanediyl group, a C3-C30 cycloalkenediyl group, a C2-C30 heterocycloalkanediyl group, and a C3-C30

heterocycloalkanediyl group in which at least one hydrogen atom is substituted with one group selected from the group consisting of a C1-C10 alkyl group, a C1-C20 haloalkyl group, and a C3-C30 cycloalkyl group or unsubstituted.

5 R_4 may be a hydrophobic group selected from the group consisting of a C1-C20 haloalkyl group, an organic silicon group, and a C3-C20 hydrocarbon group.

R_5 may be an acid labile group selected from the group

consisting of , , and . In this

10 regard, R_a , R_b , R_c and R_d may be each independently selected from the group consisting of a C1-C20 alkyl group, a C3-C30 cycloalkyl group, a (C1-C10 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C20 alkoxy group, a (C1-C10 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a
15 carboxyl group, a (C1-C10 alkyl)carboxyl group, a (C3-C18 cycloalkyl)carboxyl group, and a C3-C30 heterocycloalkyl group, or fused together between adjacent groups to form a C3-C30 saturated or unsaturated hydrocarbon ring or a C2-C30 heterocyclic group, p may be an integer of 0 to 3, and q may
20 be an integer of 0 to 10.

Here, l, m, and n are respectively numbers of the repeat units in the backbone, wherein $l+m+n=1$, $0 < l/(l+m+n) < 0.99$, $0 \leq m/(l+m+n) < 0.99$, and $0 < n/(l+m+n) \leq 0.20$.

Here, o is an integer of 0 or 1. If o is 0, R₄ is an organic silicon group, and if o is 1, R₄ is a C1-C20 haloalkyl group or a C3-C20 hydrocarbon group.

In Formula 1, R₁ and R₂ may be each independently a hydrogen atom or a C1-C4 alkyl group, preferably a hydrogen atom or a methyl group.

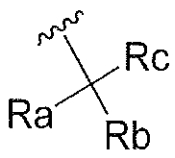
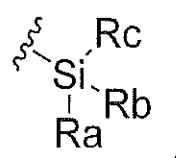
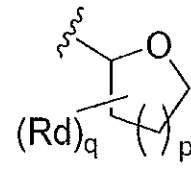
In Formula 1, R₃ may be selected from the group consisting of a C1-C10 alkanediyl group, a C2-C10 alkenediyl group, a C1-C10 heteroalkanediyl group, a C2-C10 heteroalkenediyl group, a C3-C18 cycloalkanediyl group, a C3-C18 cycloalkenediyl group, a C2-C18 heterocycloalkanediyl group, and a C3-C18 heterocycloalkanediyl group in which at least one hydrogen atom is substituted with a C1-C10 alkyl group or a C1-C10 haloalkyl group or unsubstituted. More preferably, R₃ may be selected from the group consisting of a methylene group, an ethylidene group, a 1,3-propylene group, a 1,2-propylene group, a tetramethylene group, a pentamethylene group, a 2,2-dimethylpentamethylene group, a hexamethylene group, a heptamethylene group, an octamethylene group, a nonamethylene group, a decamethylene group, a undecamethylene group, a dodecamethylene group, a tridecamethylene group, a tetradecamethylene group, a pentadecamethylene group, a hexadecamethylene group, a heptadecamethylene group, an octadecamethylene group, a nonadecamethylene group, a 1-methyl-1,3-propylene group, a

2-methyl-1,3-propylene group, a 2-methyl-1,2-propylene
 group, a 1-methyl-1,4-butylene group, a 2-methyl-1,4-
 butylene group, a methylenidene group, a propylenidene group, a
 2-propylenidene group, a 1,3-cyclobutylene group, a 1,3-
 5 cyclopentylene group, a 1,4-cyclohexylene group, a 1,5-
 cyclooctylene group, a 1,4-norbornylene group, a 2,5-
 norbornylene group, a 1,5-adamantylene group, a 2,6-
 adamantylene group, $-OCH_2-$, $-OCH(Cl)-$, $-CO-$, $-COCH_2-$, $-$
 $COCH_2CH_2-$, $-CH_2-O-CH_2-$, $-CH_2-O-CH_2CH_2-$, $-CH_2CH_2-O-CH_2-$, $-CH_2-O-$
 10 $CH_2CH_2CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-CH_2CH_2CH_2-O-CH_2-$, $-C(CH_3)_2CH_2-$,
 $-CH(CH_3)CH_2-$, $-CH(CH_2CH_3)-$, $-CH(OCH_3)-$, $-C(CF_3)(OCH_3)-$, $-CH_2-$
 $S-CH_2-$, $-CH_2-S-CH_2CH_2-$, $-CH_2CH_2-S-CH_2-$, $-CH_2-S-CH_2CH_2CH_2-$, $-$
 $CH_2CH_2-S-CH_2CH_2-$, $-CH_2CH_2CH_2-S-CH_2-$, $-CH(CH_2)CH-$, $-C(CH_2CH_2)-$,
 $-CH_2CO-$, $-CH_2CH_2CO-$, $-CH(CH_3)CH_2CO-$, $-CH(OH)-$, $-C(OH)(CH_3)-$, $-$
 15 $CH(Br)-$, $-CH(Br)CH(Br)-$, $-CH=CH-$, $-CH_2CH=CH-$, $-CH=CHCH_2-$, $-$
 $CH=CHCO-$, $-C_7H_9-$, and $-C_{10}H_{14}-$ in which at least one hydrogen
 atom is substituted with a C1-C4 alkyl group or a
 perfluoroalkyl group or unsubstituted.

In Formula 1, R_4 may be selected from the group
 20 consisting of a C1-C10 fluoroalkyl group, a silyl group, a
 C1-C10 alkylsilyl group, a C3-C10 linear or branched alkyl
 group, a C3-C14 monocyclic cycloalkyl group, a C8-C18
 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl
 group, and a C10-C30 tetracyclic cycloalkyl group, more
 25 preferably selected from the group consisting of a t-butyl

group, a trifluoromethyl group, a trimethylsilyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl group, and a heptafluoropropyl group.

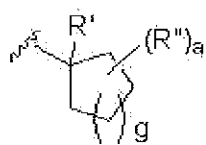
In addition, in Formula 1, R_5 may be selected from the

group consisting of , , and .

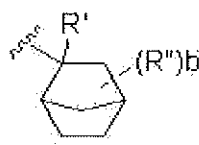
Here, R_a , R_b , R_c and R_d may be each independently selected from the group consisting of a C1-C10 alkyl group, a C3-C14 monocyclic cycloalkyl group, a C8-C20 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl group, a C10-C30 tetracyclic cycloalkyl group, a (C1-C5 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C10 alkoxy group, a (C1-C5 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C1-C5 alkyl)carboxyl group, and a (C3-C10 cycloalkyl)carboxyl group or fused together between adjacent groups to form a C6-C18 saturated or unsaturated hydrocarbon ring or a C5-C18 heterocyclic group, p may be an integer of 0 to 3, and q may be an integer of 0 to 5.

More preferably, R_5 may be selected from the group consisting of a *t*-butyl group, a trimethylsilyl group, a hydroxy-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a *t*-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl

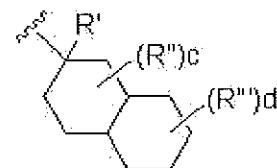
group, and groups represented by Formulae 2a to 2k below.



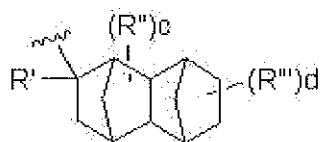
(2a)



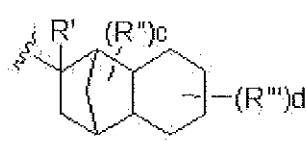
(2b)



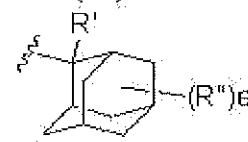
(2c)



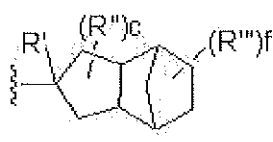
(2d)



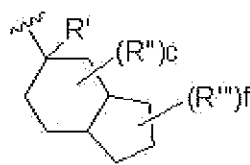
(2e)



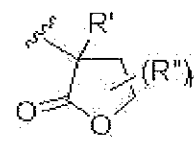
(2f)



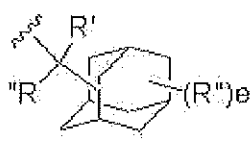
(2g)



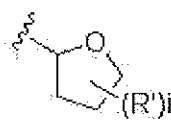
(2h)



(2i)



(2j)



(2k)

In Formulae 2a to 2k, R', R'' and R''' may be each
 5 independently a hydrogen atom or a C1-C10 alkyl group, a and
 e may be each independently an integer of 0 to 15, b may be
 an integer of 0 to 11, c and d may be are each independently
 an integer of 0 to 9, f may be an integer of 0 to 7, g and i
 may be each independently an integer of 0 to 6, h may be an
 10 integer of 0 to 4, $0 \leq c+d \leq 17$, and $0 \leq c+f \leq 15$.

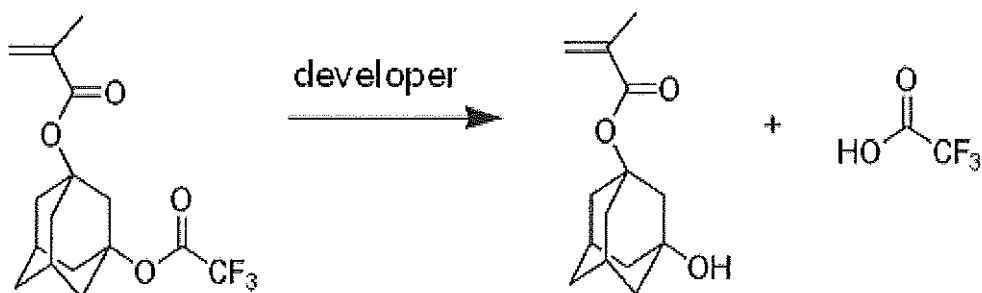
When a resist film is formed by using a resist

composition including the resist additive according to the present invention having the above-mentioned structure, the additive is dissolved in the developer with the resist at exposed regions, but the additive is converted to have hydrophilicity by a base without being dissolved in the developer at non-exposed regions. In particular, the maleic anhydride-derived repeat unit contained in the additive is ring-opened by the developer at the non-exposed regions to form carboxyl groups so that hydrophilicity of the surface of the resist film is improved. Thus, defects caused in hydrophobic surfaces may be reduced. When the resist film is formed using the resist composition including the additive, the additive is disposed on the surface of the resist film while the resist film is formed as if a separate protective film is formed on the resist film to improve hydrophobicity of the surface of the resist film, thereby preventing materials from being leached from the resist film in water during liquid immersion lithography.

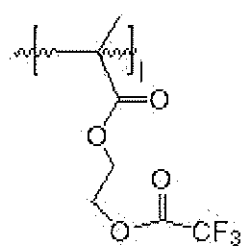
Hereinafter, each of the repeat units constituting the copolymer of the resist additive according to the present invention will be described in more detail. The acryl-derived repeat unit 1 includes a hydrophobic group having an electron withdrawing group to provide hydrophobicity to the copolymer. The copolymer is self-segregated during the preparation of the photoresist composition due to

hydrophobicity and functions as a protective film on the photoresist film to prevent leaching in water during liquid immersion lithography. In addition, the repeat unit 1 is dissolved in the developer with the resist at the exposed regions and forms a pattern with the resist without being dissolved in the developer at the non-exposed regions. However, the hydrophobic group is stripped off by a base to be converted into a hydroxyl group, as a hydrophilic group, as shown in Reaction Scheme 1 below. However, Reaction Scheme 1 below is exemplary, and the present invention is not limited thereto.

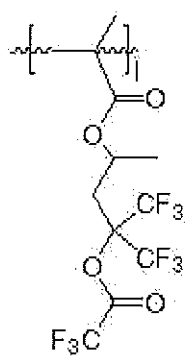
Reaction Scheme 1



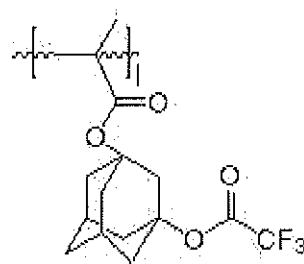
Particularly, the acryl-derived repeat unit 1 may have one of the following structures represented by Formulae 3a to 3i below.



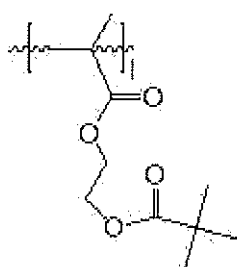
(3a)



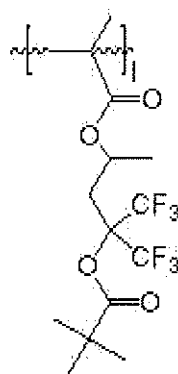
(3b)



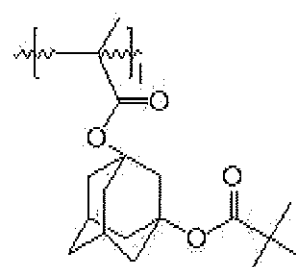
(3c)



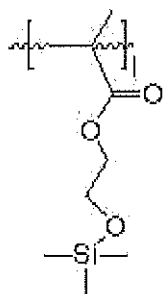
(3d)



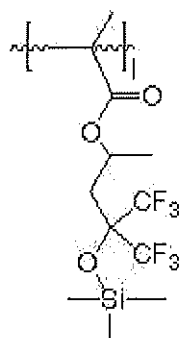
(3e)



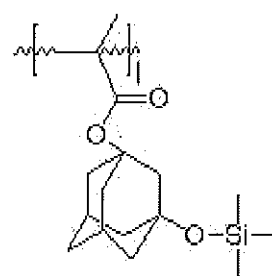
(3f)



(3g)



(3h)

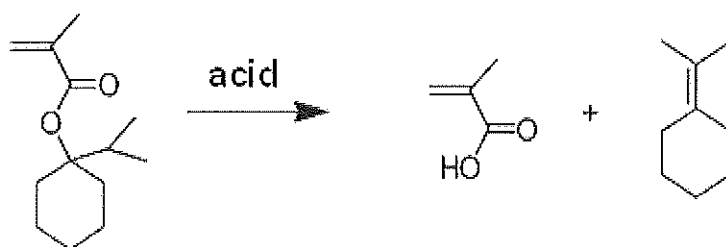


(3i)

5 An acid labile group contained at one end of another acryl-derived repeat unit *m* is converted from a hydrophobic group to a hydrophilic group acid-induced deprotection reaction at the exposed regions as shown in Reaction Scheme

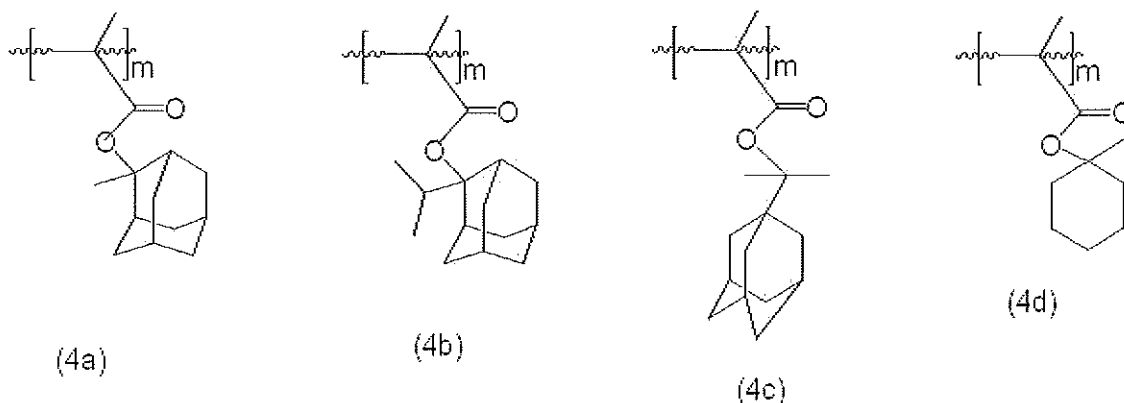
2. As a result, the additive may be easily dissolved in the developer. However, Reaction Scheme 2 below is exemplary, and the present invention is not limited thereto.

Reaction Scheme 2



5

Particularly, the acryl-derived repeat unit m may have one of the following structures represented by Formulae 4a to 4d.



10 In addition, the maleic anhydride-derived repeat unit n does not play any role at the exposed regions but is ring-opened by the developer at the non-exposed regions to form carboxyl groups as shown in Reaction Scheme 3 below, thereby improving hydrophilicity of the surface of the resist film.

15 Since the modified surface has the same characteristics as the developer, the development process is facilitated. Thus,

defects caused in hydrophobic surfaces may be reduced. However, Reaction Scheme 3 below is exemplary, and the present invention is not limited thereto.

Reaction Scheme 3



5

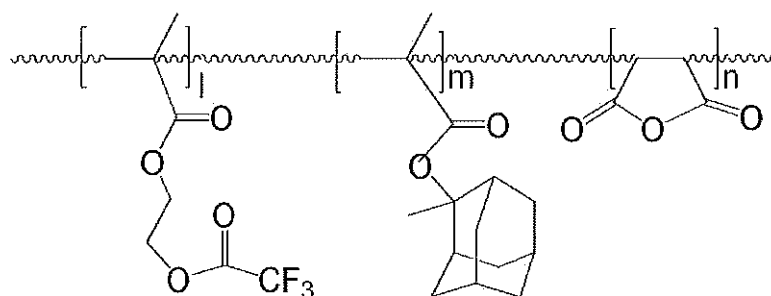
Here, l, m, and n indicate not only the content of each of the repeat units contained in the backbone of the copolymer but also substitution rates that are degrees of the dissolution of the copolymer in the developer. The copolymer according to the present invention includes the repeat units l, m and n given $l+m+n=1$, wherein $0 < l/(l+m+n) < 0.99$, $0 < m/(l+m+n) \leq 0.99$, and $0 < n/(l+m+n) < 0.20$.

When the repeat units satisfy the above conditions, the resist film may have hydrophobicity during liquid immersion lithography. Particularly, when the content of the maleic anhydride-derived repeat unit n is less than 20 mol%, a CA value may be reduced, thereby reducing defects. If the content of the maleic anhydride-derived repeat unit n is greater than 20 mol%, the additive may be dissolved by the developer at the non-exposed regions. More preferably, the content of the maleic anhydride-derived repeat unit n may be in the range of 5 to 15 mol%.

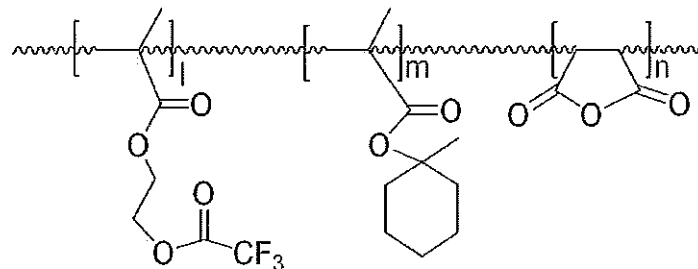
The copolymer according to the present invention having the structure shown above may be a block copolymer, a random copolymer, or a graft copolymer.

5 Examples of the copolymer may include compounds represented by Formulae 5 to 16 below. In the structural formulae, the order of the repeat units may be modified.

Formula 5

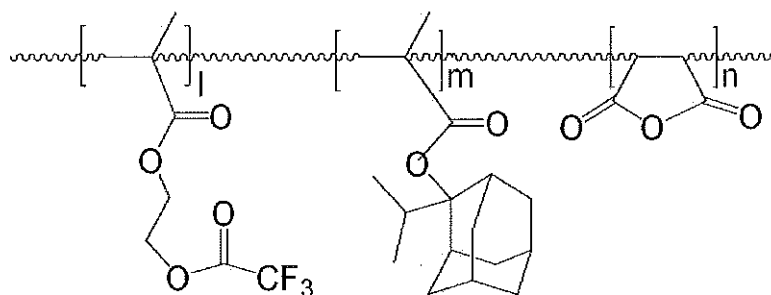


Formula 6

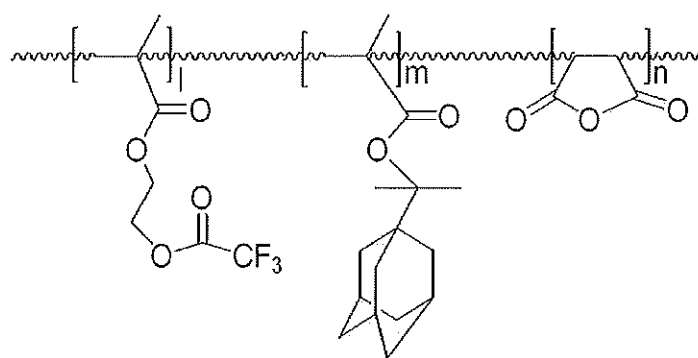


10

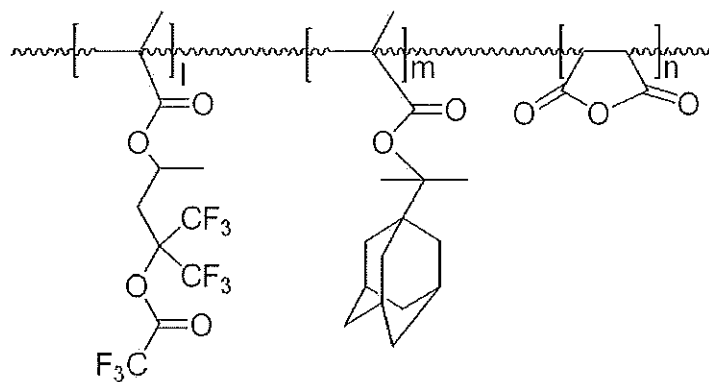
Formula 7



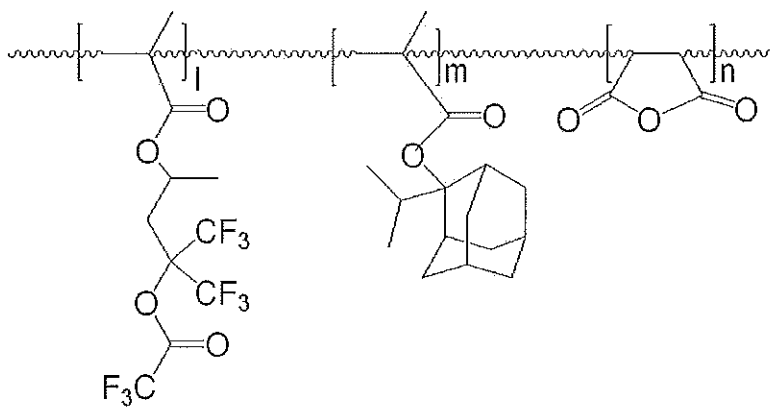
Formula 8



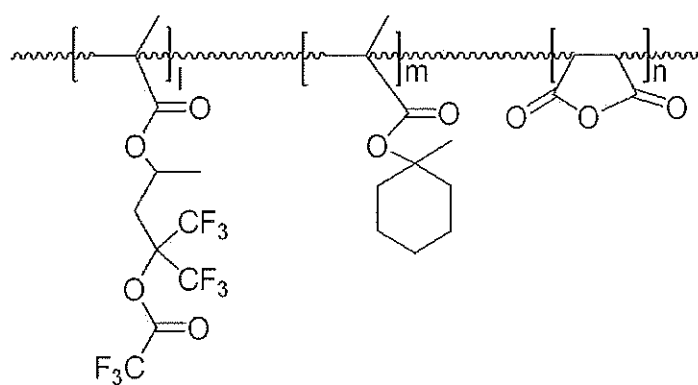
Formula 9



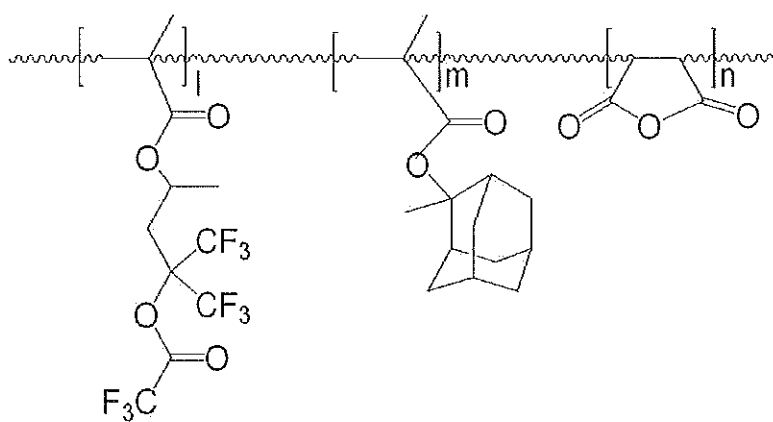
Formula 10



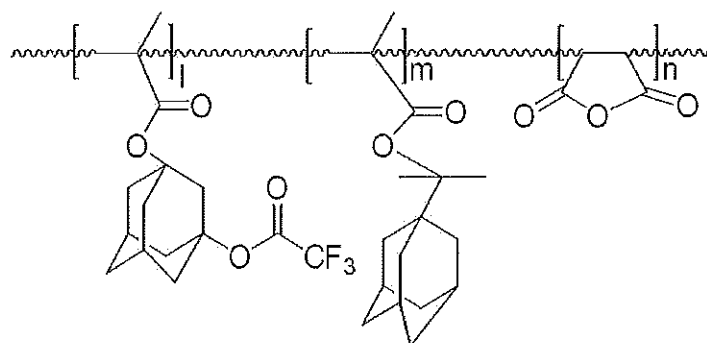
Formula 11



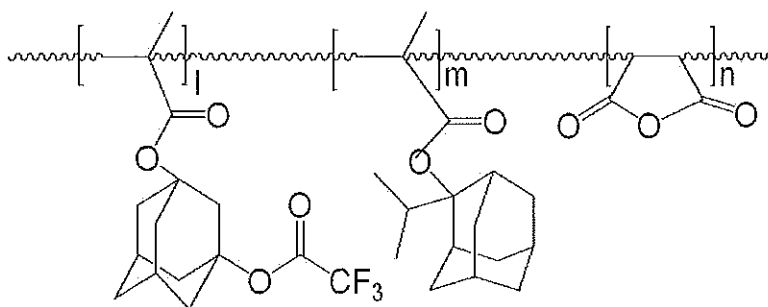
Formula 12



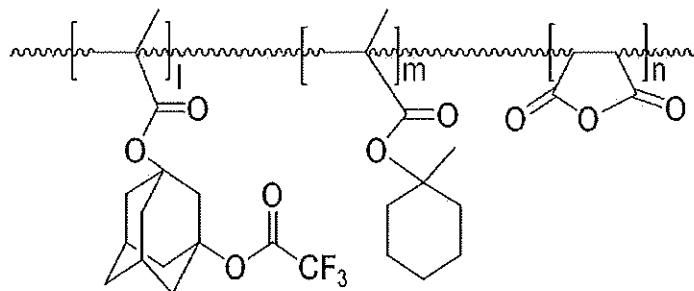
Formula 13



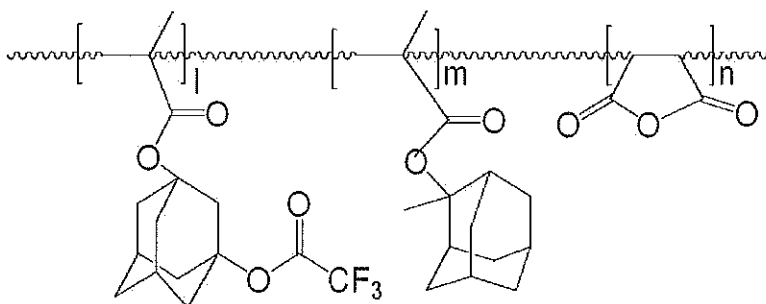
Formula 14



Formula 15



Formula 16



5 In Formulae 5 to 16, l, m, and n are respectively numbers of the repeat units in the backbone. Here, $l+m+n=1$, $0 < l/(l+m+n) < 0.99$, $0 \leq m/(l+m+n) < 0.99$, and $0 < n/(l+m+n) \leq 0.20$.

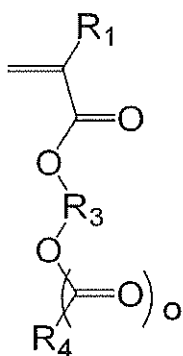
10 The copolymer according to the present invention may have a polystyrene equivalent weight average molecular weight (Mw) measured using gel permeation chromatography (GPC) in the range of 1,000 to 500,000 g/mol. If the Mw of the copolymer is too low, intermixing may occur or elution using pure water may occur during immersion lithography. On the other hand, if the Mw of the copolymer is too high, the film may not be appropriately formed or alkali solubility may be reduced. Preferably, the Mw of the copolymer may be 15 in the range of 2,000 to 100,000 g/mol to have excellent

solubility in the developer without being eluted in pure water.

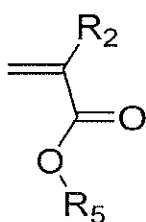
In addition, the copolymer may have a molecular weight distribution, which is a weight average molecular weight/number average molecular weight (M_w/M_n) ratio, in the
5 range of 1 to 5, more preferably 1 to 3. If the molecular weight distribution is greater than 5, line edge roughness characteristics may be deteriorated. Thus, a copolymer having M_w and molecular weight distribution within the
10 ranges described above is used as a photoresist composition providing excellent developing properties, coating properties, and thermal resistance may be obtained.

The copolymer according to the present invention having the above-mentioned structure may be prepared using
15 an acryl-based monomer represented by Formula 17 below, an acryl-based monomer represented by Formula 18 below, and a maleic anhydride monomer represented by Formula 19 below by known polymerization, such as bulk polymerization, solution polymerization, suspension polymerization, bulk and
20 suspension polymerization, and emulsion polymerization.

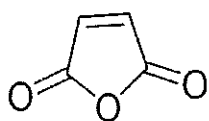
Formula 17



Formula 18



Formula 19



5

In Formulae 17 to 19, R_1 to R_5 and o are defined as described above.

Preferably, the copolymer according to the present invention may be polymerized by radical polymerization. In this regard, any radical polymerization initiator commonly used in the art, such as azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), lauryl peroxide, azobisisocapronitrile, azobisisovaleronitrile, and t-butyl hydroperoxide may be used without being limited thereto.

In addition, a polymerization solvent including at least one compound selected from the group consisting of

benzene, toluene, xylene, halogenated benzene, diethyl ether, tetrahydrofuran, esters, ethers, lactones, ketones, amides, and alcohols may be used.

During polymerization, polymerization temperature may be appropriately selected depending on the type of catalyst employed. In addition, the molecular weight distribution of the prepared polymer may be adjusted by modifying the amount of the polymerization initiator and reaction time. After polymerization is completed, unreacted monomers and byproducts remaining in the reaction mixture may be removed via solvent precipitation.

The copolymer according to the present invention prepared by adjusting the type and amount of monomers according to the preparation method described above has suitable hydrophobicity. Thus, when the resist additive is added to a resist composition, the resist film formed therefrom is transparent to exposure light and immiscible with a liquid for exposure during liquid immersion lithography, and various defects that may be caused during exposure may be reduced.

According to another embodiment of the present invention, a resist composition including the resist additive is provided.

Particularly, the resist composition includes the resist additive, a resist base polymer, an acid generator, and a solvent.

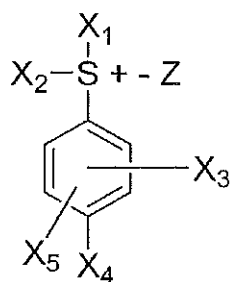
The resist additive is the same as that described above and may be contained in the resist composition in an amount ranging from 0.05 to 5% by weight based on the total weight of the resist composition. When the amount of the resist additive is within the range described above, appropriate degree of hydrophobicity is obtained, and thus a resist pattern with high resolution and sensitivity may be formed.

The resist base polymer may be any polymer used as a base resin in the formation of the resist film without limitation. Examples of the resist base polymer may include (meth)acrylic acid ester polymers, (α -trifluoromethyl)acrylic acid ester-maleic anhydride copolymers, cycloolefin-maleic anhydride copolymers, polynorbornene, cycloolefin ring-opening metathesis (ROMP) polymerization polymers, hydrogenated cycloolefin ROMP polymers, copolymers of hydroxylstyrene with one selected from the group consisting of (meth)acrylic ester derivatives, styrene, vinyl naphthalene, vinyl anthracene, vinyl pyrene, hydroxyvinyl naphthalene, hydroxyvinyl anthracene, indene, hydroxylindene, acenaphthylene, and norbornadiene, novolac resins, and mixtures thereof.

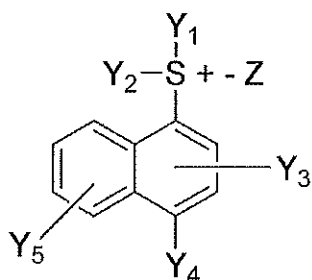
The base polymer may be contained in the resist composition in an amount in the range of 3 to 20% by weight. If the amount of the base polymer is less than 3% by weight, a film with a desired thickness may not be formed due to too low viscosity of the composition and a pattern loss may be increased due to presence of a relatively large amount of photoacid generator. On the other hand, if the amount of the base polymer is greater than 20% by weight, the film is too thick so that transmittance to radiation is decreased and a vertical pattern may not be obtained.

The acid generator, as a photoacid generator (PAG), may include onium salts such as iodonium salts, sulfonium salts, phosphonium salts, diazonium salts, pyridinium salts, or imides, preferably at least one of the sulfonium salts represented by Formulae 20 and 21, more preferably, triphenylsulfonium nonaflate.

Formula 20



Formula 21

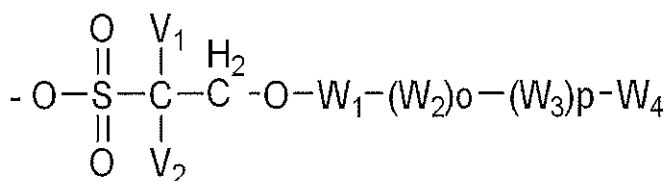


In Formulae 20 and 21, X_1 , X_2 , Y_1 and Y_2 may be each independently selected from the group consisting of a hydrogen atom, a C1-C10 alkyl group, an allyl group, a C1-C10 perfluoroalkyl group, a benzyl group, a C6-C30 aryl group, and any combination thereof. X_1 and X_2 may be fused to form a C3-C30 saturated or unsaturated hydrocarbon ring, and Y_1 and Y_2 may be fused to form a C3-C30 saturated or unsaturated hydrocarbon ring.

X_3 , X_4 , X_5 , Y_3 , Y_4 and Y_5 may be each independently selected from the group consisting of a hydrogen atom, a C1-C30 alkyl group, a halogen group, a C1-C30 alkoxy group, a C6-C30 aryl group, a thiophenoxy group, a C1-C30 thioalkoxy group, a C1-C20 alkoxy carbonyl methoxy group, and any combination thereof.

Z , which denotes an anion, may be OSO_2CF_3 , $\text{OSO}_2\text{C}_4\text{F}_9$, $\text{OSO}_2\text{C}_8\text{F}_{17}$, $\text{N}(\text{CF}_3)_2$, $\text{N}(\text{C}_2\text{F}_5)_2$, $\text{N}(\text{C}_4\text{F}_9)_2$, $\text{C}(\text{CF}_3)_3$, $\text{C}(\text{C}_2\text{F}_5)_3$, $\text{C}(\text{C}_4\text{F}_9)_3$, or a functional group represented by Formula 22 below.

Formula 22



In Formula 22, V_1 and V_2 may be each independently a halogen atom.

W_1 may be $-(C=O)-$ or $-(SO_2)-$.

W_2 may be a C1-C10 alkanediyl group.

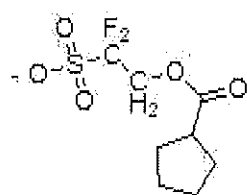
5 W_3 may be selected from the group consisting of a C3-C30 cycloalkyl group, a C6-C30 aryl group, a C7-C30 aralkyl group, a C6-C30 aryloxy group, a C6-C30 arylthio group, and a C5-C30 heterocyclic group.

10 W_4 may be selected from the group consisting of a hydrogen atom, a halogen group, a C1-C10 alkyl group, a C1-C10 alkoxy group, a C1-C10 haloalkyl group, a C1-C10 alkylthio group, a C6-C30 aryl group, and any combination thereof.

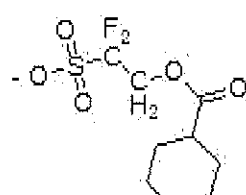
15 Here, o may be an integer of 0 to 1, and p may be an integer of 0 to 2.

20 In the acid generator, a diffusion length of acid in a resist film may be appropriately maintained short and the resist film may have high transmittance by introducing a cyclic alkyl group to the anions. As a result, a resist with high resolution may be obtained.

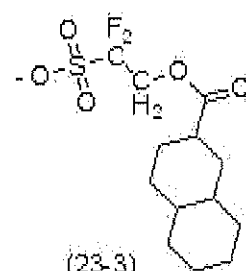
Preferably, Z which denotes an anion, in Formula 22 may be selected from the group consisting of functional groups represented by Formulae 23-1 to 23-36 below.



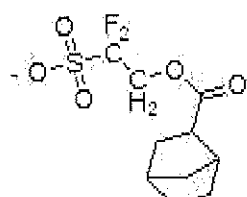
(23-1)



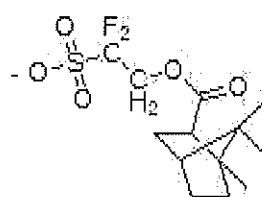
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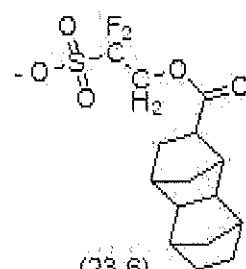
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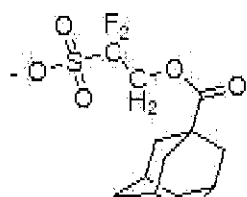
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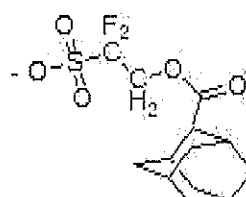
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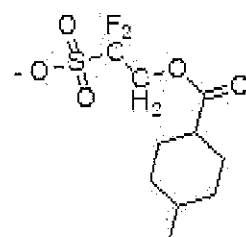
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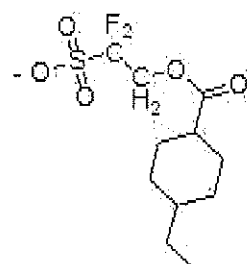
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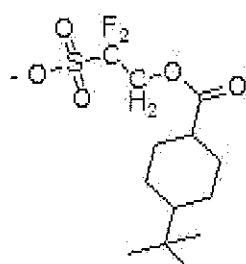
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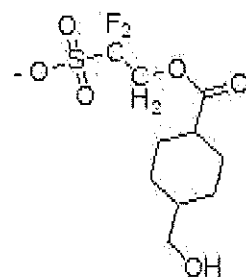
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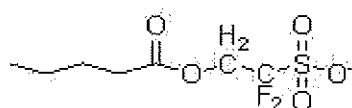
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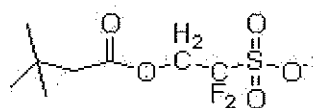
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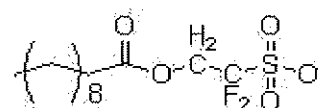
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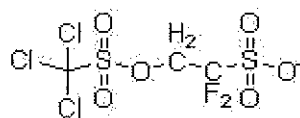
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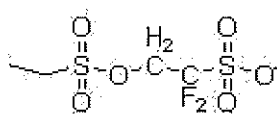
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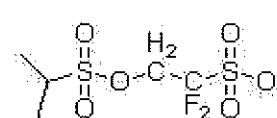
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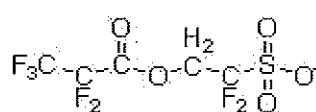
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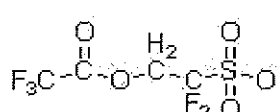
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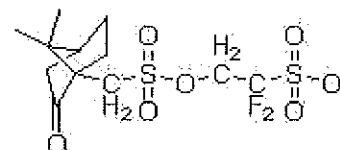
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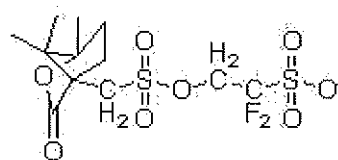
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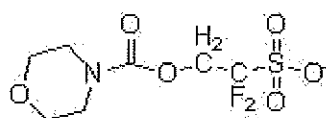
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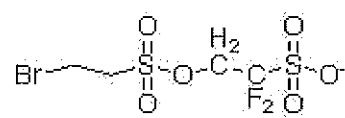
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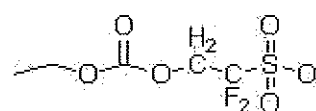
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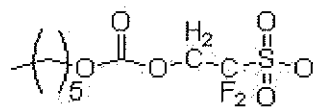
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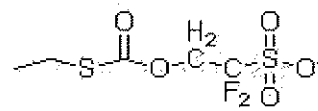
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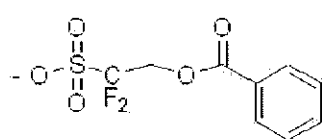
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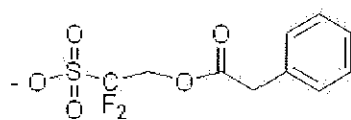
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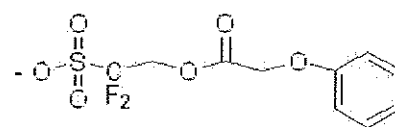
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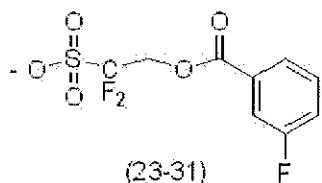
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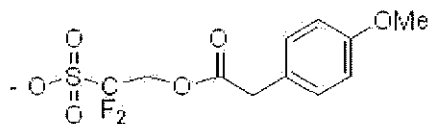
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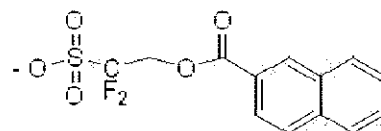
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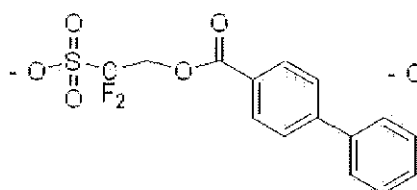
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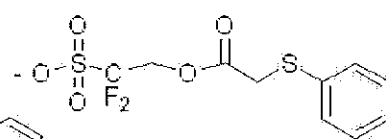
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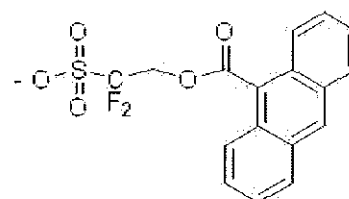
(23-33)



(23-34)

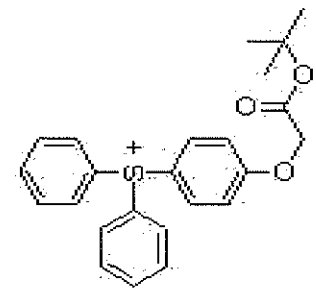
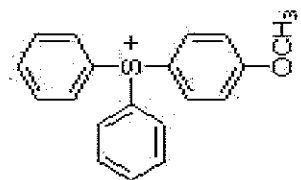
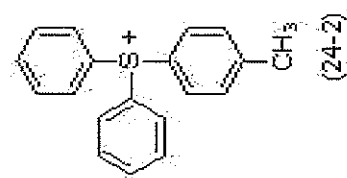
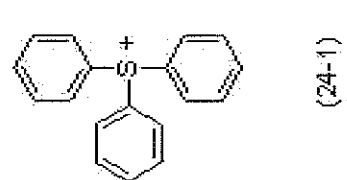


(23-35)



(23-36)

In addition, in Formulae 20 and 21, a cationic portion may be represented by Formulae 24-1 to 24-16 below.



The acid generators may be used alone or in combination of at least two thereof. In addition, the amount of the acid generator may be in the range of 0.3 to 15 parts by weight, preferably 0.5 to 10 parts by weight, more preferably 2 to 10 parts by weight based on 100 parts by weight of polymer solids. If the amount of the acid generator is greater than 15 parts by weight, verticality of a pattern may significantly decrease. On the other hand, if the amount of the acid generator is less than 0.3 parts by weight, flexibility of a pattern may be deteriorated.

In order to uniformly and smoothly coat the resist composition, the polymer and the acid generator may be dissolved in a solvent having an appropriate evaporation rate and viscosity. Examples of the solvent may include: esters such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, methylcellosolve acetate, ethylcellosolve acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, and propylene glycol monopropyl ether acetate; and ketones such as methyl isopropyl ketone, cyclohexanone, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, 2-heptanone, ethyl lactate, and γ -butyrolactone. These solvents may be used alone or in combination of at least two thereof.

The amount of the solvent may be appropriately adjusted according to physical properties of the solvent, i.e., volatility, viscosity, and the like.

5 The resist composition according to the present invention may also include additives depending on application such as improvement of coating properties.

10 The additive may be any additive commonly used in resist compositions without limitation. Examples of the additive may include an alkali soluble quencher, an acid diffusion quencher, a surfactant, and a sensitizer, and the additives may be used alone or in combination of at least two thereof.

15 The alkali soluble quencher may be any alkali soluble quencher commonly used in resist compositions. Examples of the alkali soluble quencher may include phenol or carboxylic acid derivatives.

20 The acid diffusion quencher suppresses diffusion of acid generated by the acid generator during exposure to the resist film and chemical reaction in non-exposed regions. Through use of the acid diffusion quencher, storage stability of radiosensitive resin compositions may be improved, resolution of the resist may be improved, and line width variation of the resist pattern during a period from exposure to development may be inhibited.

The acid diffusion quencher may be a basic compound. Examples of the acid diffusion quencher may include: amines such as ammonia, methylamine, isopropylamine, n-hexylamine, cyclopentylamine, methylenediamine, ethylenediamine, dimethylamine, diisopropylamine, diethylenediamine, N,N-dimethylmethylenediamine, N,N-dimethylethylenediamine, trimethylamine, triethylamine, N,N,N',N'-tetramethylmethylenediamine, N,N,N',N'-tetramethylethylenediamine, tetramethyltetraethylenepentamine, dimethylethylamine, methylethylpropylamine, benzylamine, phenethylamine, benzyldimethylamine, tetramethyl ammonium hydroxide, aniline, N,N-dimethyltoluidine, triphenylamine, phenylenediamine, pyrrole, oxazole, isooxazole, thiazole, isothiazole, imidazole, pyrazole, pyrroline, pyrrolidine, imidazoline derivatives, imidazolidine derivatives, pyridine derivatives, pyridazine derivatives, pyrimidine derivatives, pyrazine derivatives, pyrazoline derivatives, pyrazolidine derivatives, piperidine derivatives, piperazine derivatives, and morpholine; nitrogen-containing compounds such as aminobenzoic acid, indolecarboxylic acid, amino acid derivatives (e.g., nicotinic acid, alanine, arginine, and aspartic acid), 3-pyridinesulfonic acid, p-pyridinium toluenesulfonate, 2-hydroxypyridine, amino cresol, 2,4-quinolinediol, 2-(2-hydroxyethyl)pyridine, and 1-(2-

hydroxyethyl)piperazine; amide derivatives such as formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionic amide, and benzamide; or imide derivatives such as phthalimide, succinimide, and maleimide.

The amount of the basic compound may be in the range of 0.01 to 5 parts by weight, preferably, 0.1 to 1 parts by weight, based on 100 parts by weight of polymer solids. If the amount of the basic compound is less than 0.01 parts by weight, the pattern may be deformed as a delay time after exposure increases. On the other hand, if the amount of the basic compound is greater than 5 parts by weight, resolution and sensitivity may be deteriorated.

The surfactant is used to improve coating properties, developing properties, and the like. Examples of the surfactant may include polyoxyethylenelaurylether, polyoxyethylenestearylether, polyoxyethylene, and polyethyleneglycoldilaurate, but are not limited thereto.

A resist pattern that is formed using the resist composition according to the present invention has improved line width roughness characteristics and high resolution in both C/H and L/S patterns. In addition, a wide process window provides an excellent pattern profile regardless of the type of the substrate and improved contrast. Accordingly, the resist composition is useful as a positive

chemically amplified photoresist composition having
photosensitivity to far ultraviolet light such as is
produced by a KrF excimer laser, ArF excimer laser, or F₂
excimer laser, X-rays such as synchrotron radiation, and
5 charged particle rays such as extreme ultraviolet (EUV).

According to another embodiment of the present
invention, a method of forming a resist pattern using the
resist composition is provided.

Particularly, the method includes forming a resist
10 film by coating the resist composition on a substrate,
heating the resist film and exposing the resist film to
light to form a predetermined pattern, and developing the
exposed pattern.

The substrate may be a wafer substrate, and the
15 coating may be performed on the substrate via spin coating,
flown coating, roll coating, or the like.

Particularly, the resist composition is coated on the
substrate such as a silicon wafer to a thickness in the
range of 0.3 to 2.0 μm , and the coating is pre-baked at 60
20 to 150°C for 1 to 10 minutes, preferably at 80 to 130°C for 1
to 5 minutes.

Then, the resist film is partially exposed to
radiation in order to form a micropattern. In this regard,
examples of the radiation may include ultraviolet light such
25 as I-line, far ultraviolet light such as is produced by a

KrF excimer laser, ArF excimer laser, and F₂ excimer laser, X-rays, and charged particle rays such as electron beams, but are not limited thereto. The radiation may be appropriately adjusted according to the type of the acid generator.

Particularly, exposure is performed in an exposure dose of about 1 to about 200 mJ/m², preferably about 10 to about 100 mJ/m². This is followed by post exposure baking (PEB) at 60 to 150°C for 1 to 5 minutes, preferably at 80 to 130°C for 1 to 3 minutes.

After exposure, the exposed resist pattern is developed with a developer for 0.1 to 3 minutes, preferably 0.5 to 2 minutes by any conventional techniques such as dip, puddle, and spray techniques. As a result, a desired pattern is formed on the substrate. The developer may be an aqueous solution including sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium methasilicate, ammonia, ethylamine, n-propylamine, triethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, or the like, preferably tetramethylammonium hydroxide.

Optionally, the developer may further include additives such as a surfactant or water soluble alcohols.

According to the method of forming the pattern using the resist composition according to the present invention, a

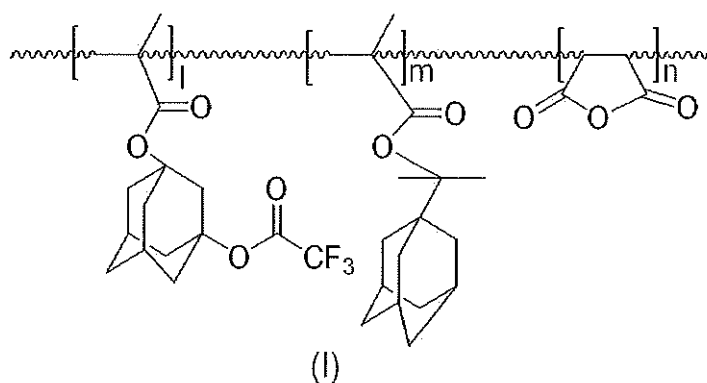
micro resist pattern with excellent sensitivity and high resolution may be obtained.

Hereinafter, the present invention will be described more fully with reference to the following examples.

Preparation Example: Synthesis of Polymer

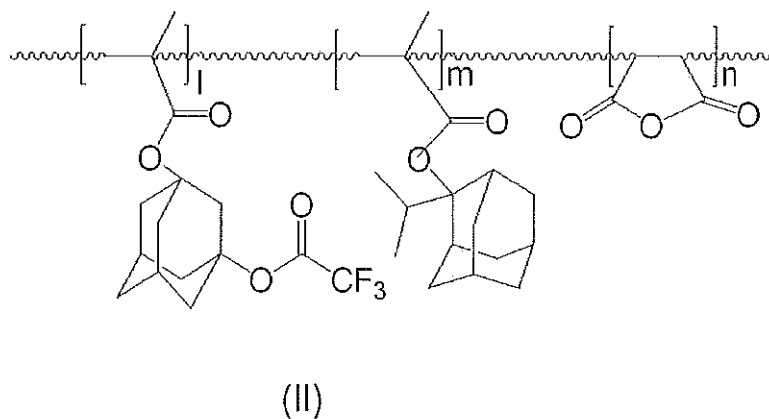
Polymer Synthesis Example 1

A solution prepared by dissolving 10 g of 2-methyl-acrylic acid 3-(2,2,2-trifluoro-acetoxy)-adamantan-1-yl ester, 1 g of maleic anhydride 1g, and 15 g of 2-methyl-acrylic acid 1-isopropyl-cyclohexyl ester in 255 g of 1,4-dioxane and 1 g of dimethyl azobis butyronitrile (DMAB), as an initiator, were added to a jacket reactor and stirred. The temperature of the reactor was gradually increased by setting the temperature of a circulator to 65°C, and the reactor was stirred at 65°C for 8 hours. After reaction was terminated, the reaction solution was precipitated by adding 3.4 L of n-hexane thereto. The precipitates were filtered and dried in vacuum to obtain Polymer I represented by the following formula. A polystyrene equivalent weight average molecular weight (Mw) of Polymer I was 7,500 g/mol.



Polymer Synthesis Example 2

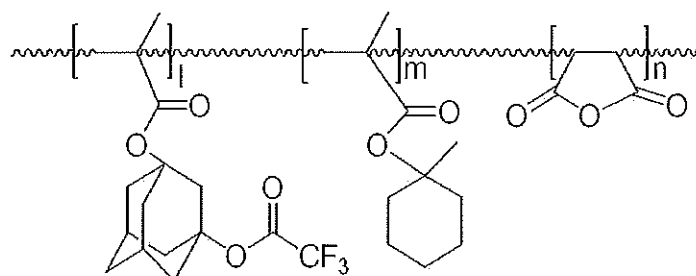
Polymer II represented by the following formula was prepared in the same manner as in Polymer Synthesis Example 1, except that 2-methyl-acrylic acid 2-isopropyl-adamantan-2-yl ester was used instead of 2-methyl-acrylic acid 1-isopropyl-cyclohexyl ester in Polymer Synthesis Example 1. A polystyrene equivalent Mw of Polymer II was 8,000 g/mol.



Polymer Synthesis Example 3

Polymer III represented by the following formula was prepared in the same manner as in Polymer Synthesis Example 1, except that 2-methyl-acrylic acid 1-methyl-cyclohexyl

ester was used instead of 2-methyl-acrylic acid 1-isopropyl-cyclohexyl ester in Polymer Synthesis Example 1. A polystyrene equivalent Mw of Polymer III was 9,200 g/mol.



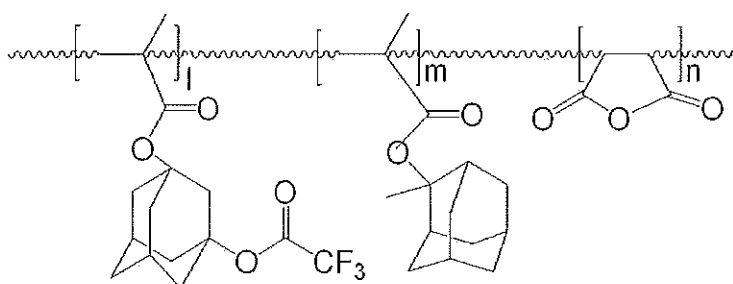
(III)

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Polymer Synthesis Example 4

Polymer IV represented by the following formula was prepared in the same manner as in Polymer Synthesis Example 1, except that 2-methyl-acrylic acid 2-methyl-adamantan-2-yl ester was used instead of 2-methyl-acrylic acid 1-isopropyl-cyclohexyl ester in Polymer Synthesis Example 1. A polystyrene equivalent Mw of Polymer IV was 7,100 g/mol.

10

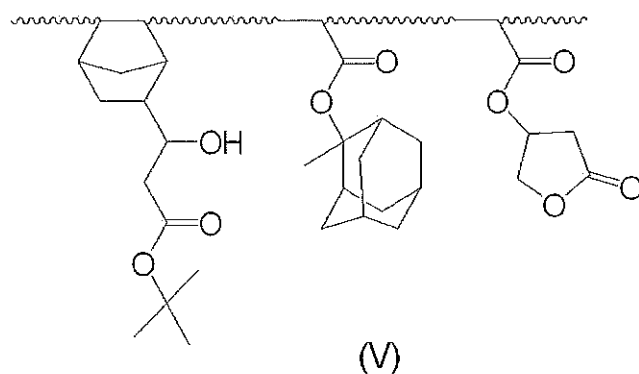


(IV)

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Evaluation Example 1: Evaluation of Hydrophobicity of Additive

1.0 g of each of the polymers synthesized in Polymer Synthesis Examples 1 to 4 was dissolved in 25 g of 4-methyl pentanol, and the solution was filtered using a 0.2 μm polypropylene filter to prepare resist protective film compositions. For comparison with the additive according to the present invention in terms of effect, Polymer V represented by the following formula was used in Comparative Example 1.



Each of the prepared resist protective film compositions was spin-coated onto a silicon substrate and baked at 100 $^{\circ}\text{C}$ for 60 seconds to form resist protective films with a thickness of 50 nm.

Sliding angles and receding contact angles of the resist protective films were respectively measured.

Specifically, 50 μl of pure water was dropped to form a droplet on the silicon substrate provided with the resist protective film which was kept horizontal. While the silicon substrate was gradually inclined, the angle (sliding

angle) at which the droplet started sliding down was measured as well as the receding contact angle. Results are shown in Table 1 below.

Table 1

	Polymer as resist additive	Sliding angle before development (°)	Receding contact angle before development (°)	Sliding angle after development (°)	Receding contact angle after development (°)
Synthesis Example 1	Polymer I	92.4	69.5	78.9	28.8
Synthesis Example 2	Polymer II	94.2	80.1	79.6	43.6
Synthesis Example 3	Polymer III	94.6	80.8	77.9	45.5
Synthesis Example 4	Polymer IV	95.6	81.3	75	43.6
Comparative Example 1	Polymer V	89.7	69.1	84.9	66

5

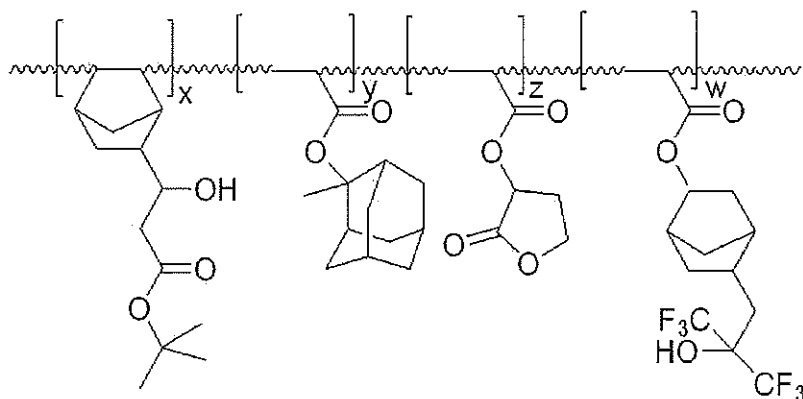
Referring to Table 1, resist protective films including the polymers prepared in Polymer Synthesis Examples 1 to 4 have high water repellency, low solubility in water, and high solubility in alkali solutions, and may be easily removed by an alkali developer during development. In addition, it was identified that the sliding angle or receding contact angle of the polymers prepared in Polymer Synthesis Examples 1 to 4 were not negatively influenced.

Experimental Example: Formation of Resist Film and Measurement of Characteristics of Resist Film

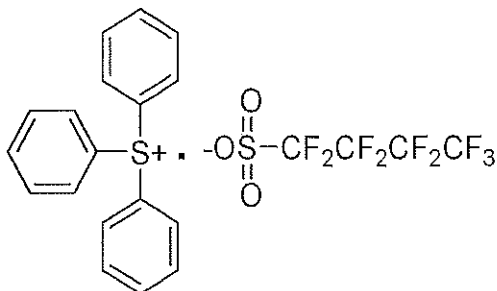
Examples 1 to 4

5 g of a resist polymer represented by Formula 20 below (Mw: 8,500 g/mol, Mw/Mn: 1.75, and a molar ratio of the repeat units: x:y:z:w=1:1:1:1), 1.0 g of each of the polymers prepared in Polymer Synthesis Examples 1 to 5, 0.31 g of a photoacid generator represented by Formula 21 below, and 0.07 g of triisopropanol amine, as a quencher, were added to 80 g of propylene glycol monoethyl ether acetate (PGMEA), and the solution was filtered using a 0.2 μ m polypropylene filter to form photoresist film compositions.

Formula 25



Formula 26



A bottom anti-reflective coating (BARC) with a thickness of 90 nm was formed on a silicon substrate, and a photoresist film composition prepared as described above was

coated on the substrate provided with the BARC. The substrate was backed at 110° for 60 seconds to form a photoresist film with a thickness of 120 nm.

Then, in order to realize liquid immersion lithography, exposed films were rinsed with pure water for 5 minutes. That is, exposure was performed using an ArF scanner 306C (Nikon Corp., NA=0.78, 6% halftone mask) and the substrate was rinsed with pure water for 5 minutes. The exposure was performed at 110° for 60 seconds, a PEB was performed, and a development was performed using 2.38% by weight of TMAH developer for 60 seconds.

Comparative Example 2

A resist film was formed in the same manner as in Example 1, except that the resist additive was not used.

The silicon substrates provided with the resist films prepared in Examples 1 to 4 and Comparative Example 2 were cut to evaluate sensitivity. The sensitivity corresponded to an exposure dose used to form a 65 nm line-and-space (L/S) pattern at a resolution of 1:1. Results are shown in Table 2 below.

Table 2

	Polymer as resist additive	Sensitivity (mJ/cm ²)
Example 1	Polymer I	48
Example 2	Polymer II	50.1
Example 3	Polymer III	49.9
Example 4	Polymer IV	54.3

Comparative Example 2	Polymer V	Not measurable at 65 nm
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Referring to Table 2, when a resist film not including a protective film was formed as described in Comparative Example 2 and rinsed with pure water after exposure, a T-top shape resist pattern was formed since generated acid was dissolved in water. However, the resist patterns were not deformed in Examples 1 to 4 using the polymers prepared in Synthesis Examples 1 to 4 as resist additives.

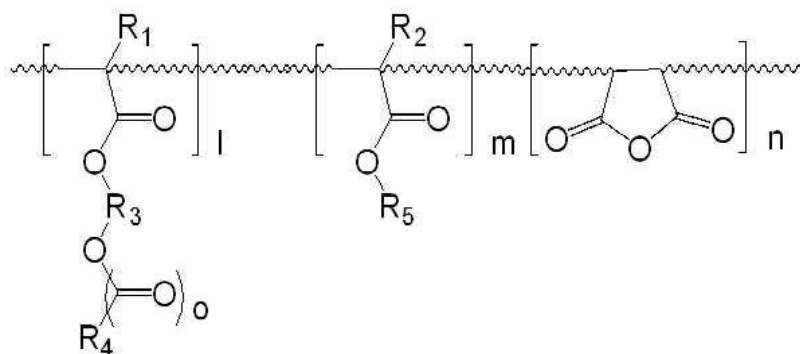
As is apparent from the above description, the present invention provides a resist additive capable of improving hydrophobicity of the surface of a resist film when added to a resist composition to prevent leaching in water during exposure of an immersion lithography process and capable of forming a micro resist pattern with excellent sensitivity and high resolution.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

WHAT IS CLAIMED IS:

1. A resist additive represented by Formula 1 below:

Formula 1

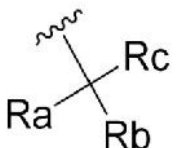
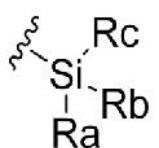
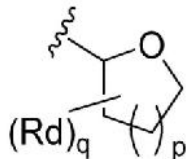


wherein R_1 and R_2 are each independently a hydrogen atom or a C1-C8 alkyl group,

R_3 is selected from the group consisting of a C1-C20 alkanediyl group, a C2-C20 alkenediyl group, a C1-C20 heteroalkanediyl group, a C2-C20 heteroalkenediyl group, a C3-C30 cycloalkanediyl group, a C3-C30 cycloalkenediyl group, a C2-C30 heterocycloalkanediyl group, and a C3-C30 heterocycloalkanediyl group in which at least one hydrogen atom is substituted with one group selected from the group consisting of a C1-C10 alkyl group, a C1-C20 haloalkyl group, and a C3-C30 cycloalkyl group or unsubstituted,

R_4 is a hydrophobic group selected from the group consisting of a C1-C20 haloalkyl group,

R₅ is an acid labile group selected from the group

consisting of , , and , wherein

R_a, R_b, R_c and R_d are each independently selected from the group consisting of a C1-C20 alkyl group, a C3-C30 cycloalkyl group, a (C1-C10 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C20 alkoxy group, a (C1-C10 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C1-C10 alkyl)carboxyl group, a (C3-C18 cycloalkyl)carboxyl group, and a C3-C30 heterocycloalkyl group, or fused together between adjacent groups to form a C3-C30 saturated or unsaturated hydrocarbon ring or a C2-C30 heterocyclic group, p is an integer of 0 to 3, and q is an integer of 0 to 10,

l, m, and n are respectively numbers of the repeat units in a backbone, wherein l+m+n=1, 0<l/(l+m+n)<0.99, 0≤m/(l+m+n)<0.99, and 0<n/(l+m+n)≤0.20, and

o is an integer of 1.

2. The resist additive of claim 1, wherein R₃ is selected from the group consisting of a C1-C10 alkanediyl group, a C2-C10 alkenediyl group, a C1-C10 heteroalkanediyl group, a C2-C10 heteroalkenediyl group, a C3-C18 cycloalkanediyl group, a C3-C18 cycloalkenediyl

group, a C2-C18 heterocycloalkanediyl group, and a C3-C18 heterocycloalkanediyl group in which at least one hydrogen atom is substituted with a C1-C10 alkyl group or a C1-C10 haloalkyl group or unsubstituted.

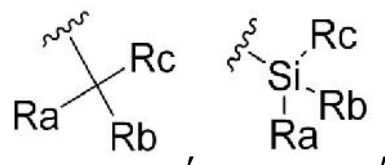
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3. The resist additive of claim 1, wherein R₄ is a C1-C10 fluoroalkyl group.

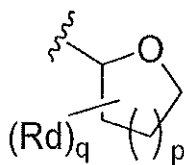
10 4. The resist additive of claim 1, wherein R₄ is selected from the group consisting of a trifluoromethyl group, a di(trifluoromethyl)isopropyl group, a pentafluoroethyl group, and a heptafluoropropyl group.

5. The resist additive of claim 1, wherein R₅ is

15 selected from the group consisting of

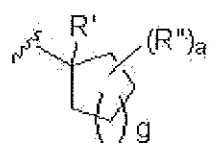


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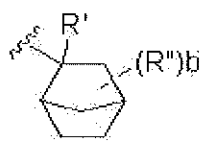


and $(R_d)_q$, wherein R_a , R_b , R_c and R_d are each independently selected from the group consisting of a C1-C10 alkyl group, a C3-C14 monocyclic cycloalkyl group, a C8-C20 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl group, a C10-C30 tetracyclic cycloalkyl group, a (C1-C5 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C10 alkoxy group, a (C1-C5 alkoxy)alkyl group, an acetyl group, an acetylalkyl group, a carboxyl group, a (C1-C5 alkyl)carboxyl group, and a (C3-C10 cycloalkyl)carboxyl group or fused together between adjacent groups to form a C6-C18 saturated or unsaturated hydrocarbon ring or a C5-C18 heterocyclic group, p is an integer of 0 to 3, and q is an integer of 0 to 5.

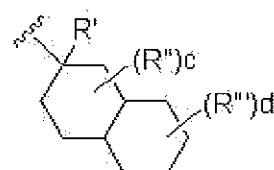
6. The resist additive of claim 1, wherein R_5 is selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxy-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by Formulae 2a to 2k below:



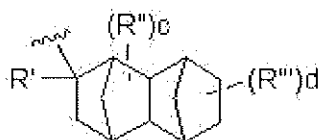
(2a)



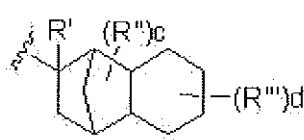
(2b)



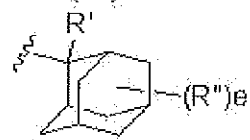
(2c)



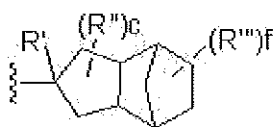
(2d)



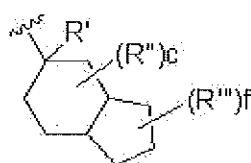
(2e)



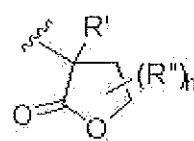
(2f)



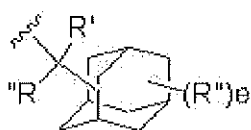
(2g)



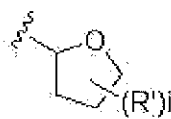
(2h)



(2i)



(2j)

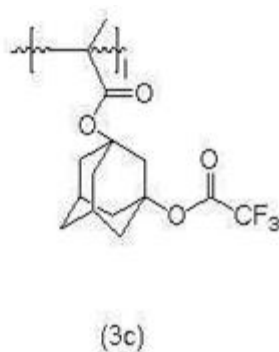
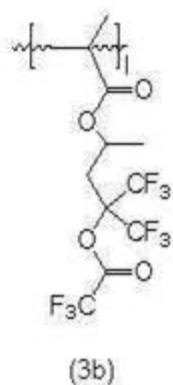
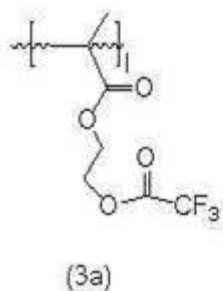


(2k)

wherein R', R'' and R''' are each independently a hydrogen atom or a C1-C10 alkyl group, a and e are each independently an integer of 0 to 15, b is an integer of 0 to 11, c and d are each independently an integer of 0 to 9, f is an integer of 0 to 7, g and i are each independently an integer of 0 to 6, h is an integer of 0 to 4, $0 \leq c+d \leq 17$, and $0 \leq c+f \leq 15$.

7. The resist additive of claim 1, wherein a repeat unit 1 is selected from the group consisting of

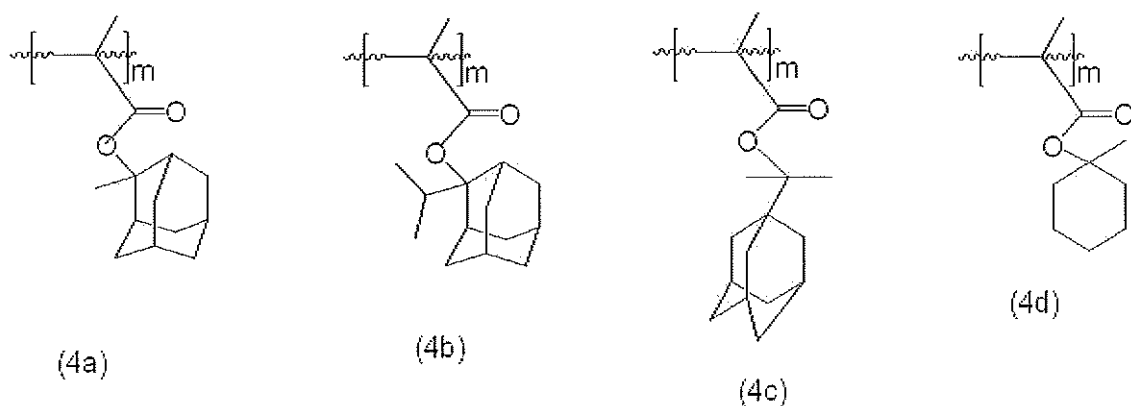
repeat units represented by Formulae 3a to 3c below:



8. The resist additive of claim 1, wherein a
 5 repeat unit m is selected from the group consisting of
 repeat units represented by Formulae 4a to 4d below:

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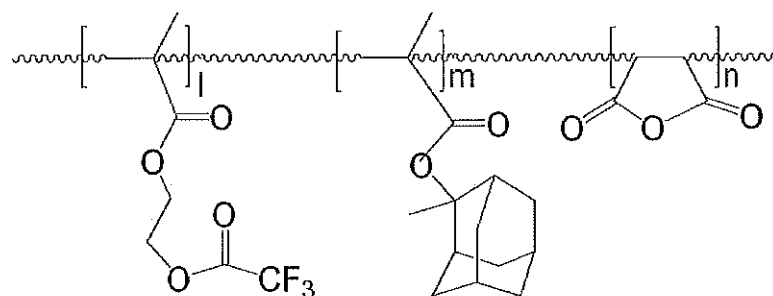
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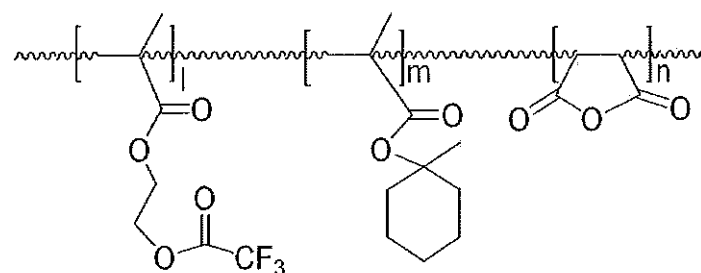
9. The resist additive of claim 1, wherein a repeat unit n of Formula 1 is comprised in a copolymer of the resist additive in an amount of 5 to 15 mol%.

10. The resist additive of claim 1, wherein the resist additive is selected from the group consisting of compounds represented by Formulae 5 to 16 below:

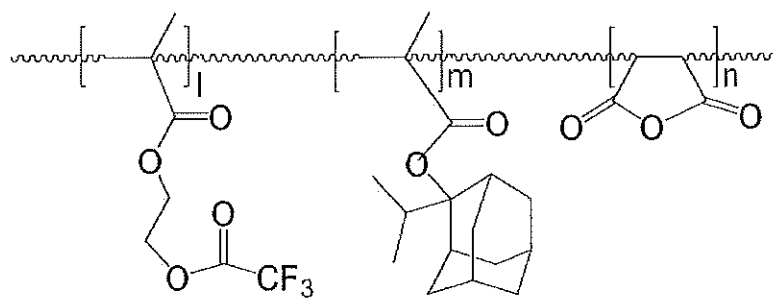
Formula 5



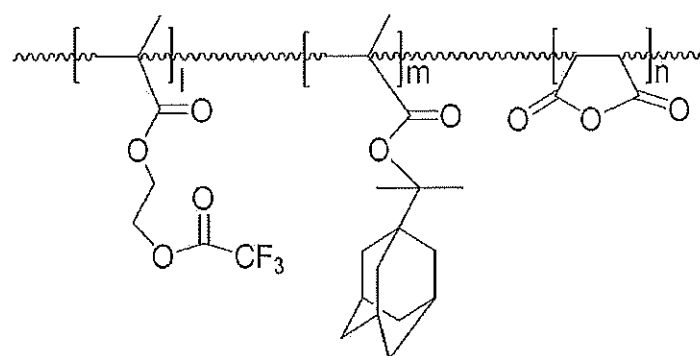
Formula 6



Formula 7

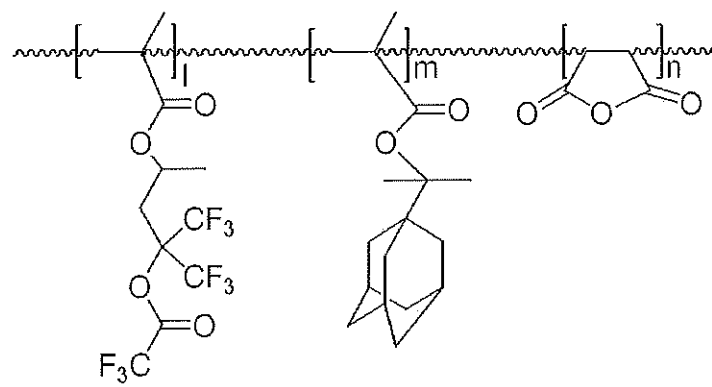


Formula 8

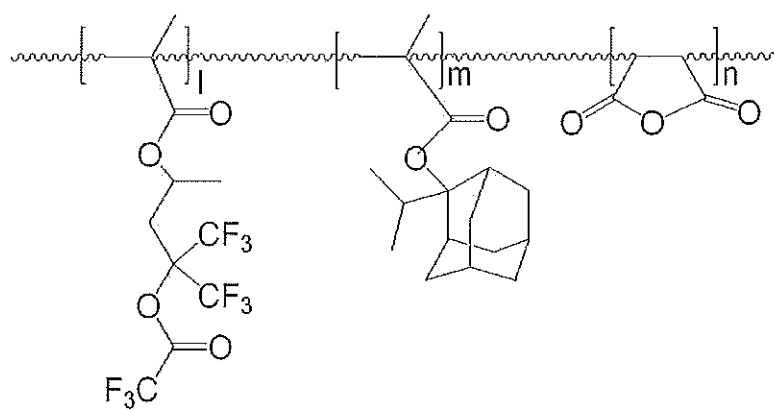


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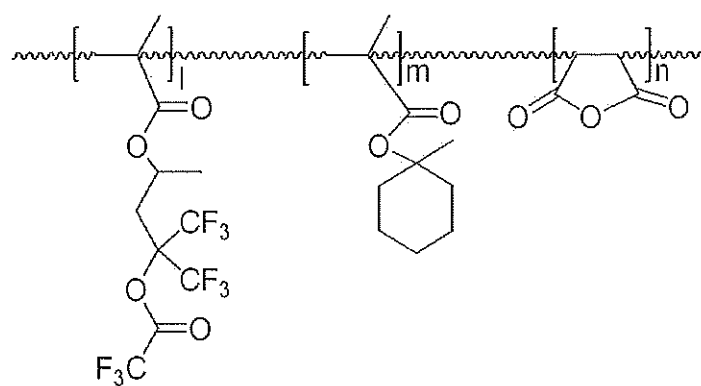
Formula 9



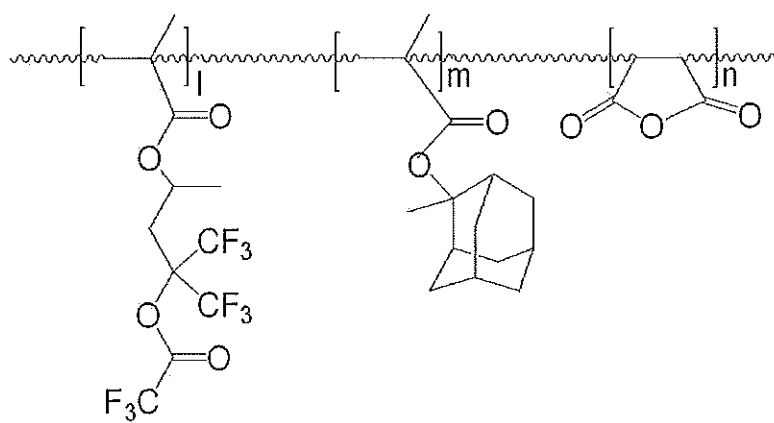
Formula 10



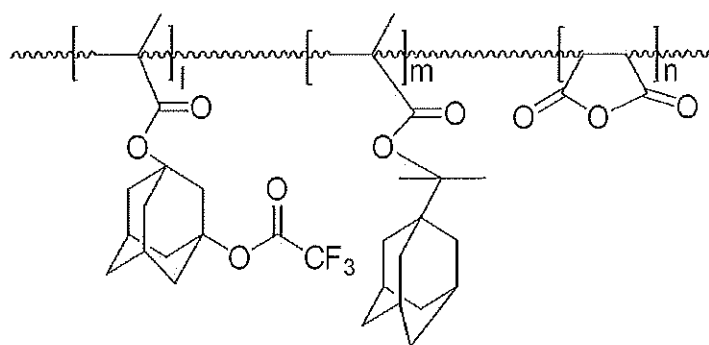
Formula 11



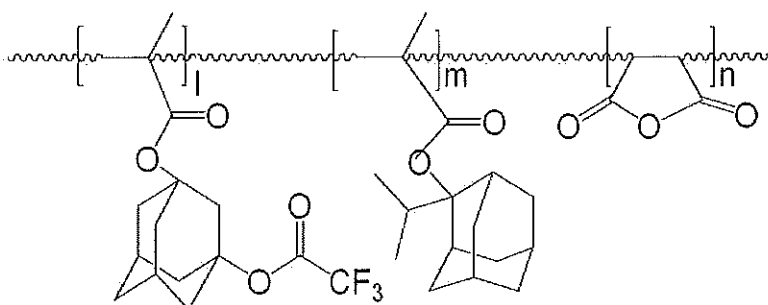
Formula 12



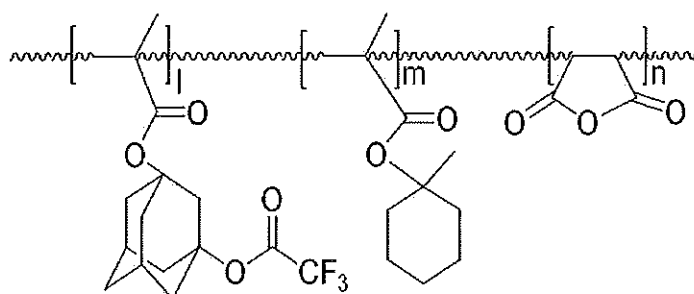
Formula 13



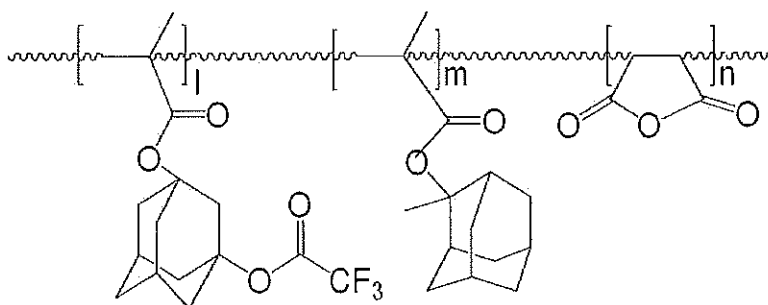
Formula 14



Formula 15



Formula 16



wherein l , m , and n are respectively numbers of the repeat units in a backbone, wherein $l+m+n=1$,

$0 < l/(1+m+n) < 0.99$, $0 \leq m/(1+m+n) < 0.99$, and $0 < n/(1+m+n) \leq 0.20$.

11. The resist additive of claim 1, wherein a polystyrene equivalent weight average molecular weight of the resist additive measured using gel permeation chromatography is in the range of 1,000 to 500,000 g/mol.

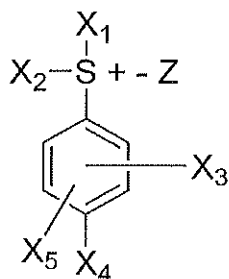
12. The resist additive of claim 1, wherein a weight average molecular weight/number average molecular weight ratio of the resist additive is in the range of 1 to 5.

13. A resist composition comprising a resist additive according to any one of claims 1 to 12, a resist base polymer, an acid generator, and a solvent.

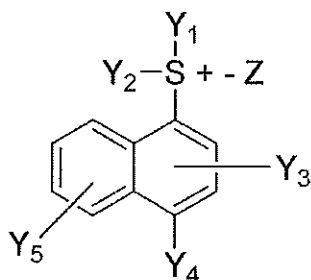
14. The resist composition of claim 13, wherein the amount of the resist additive is in the range of 0.05 to 5% by weight based on the total weight of the resist composition.

15. The resist composition of claim 13, wherein the acid generator comprises at least one compound selected from the group consisting of compounds represented by Formulae 20 and 21 below:

Formula 20



Formula 21

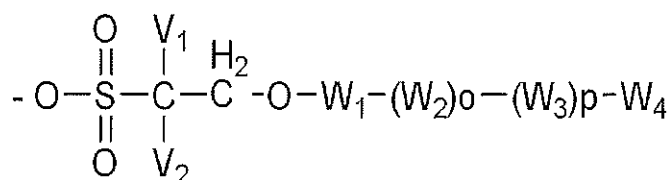


5 wherein X_1 , X_2 , Y_1 , and Y_2 are each independently
 selected from the group consisting of a hydrogen atom, a
 C1-C10 alkyl group, an allyl group, a perfluoroalkyl
 group, a benzyl group, a C6-C30 aryl group, and any
 combination thereof, wherein X_1 and X_2 are fused to form a
 10 C3-C30 saturated or unsaturated hydrocarbon ring, and Y_1
 and Y_2 are fused to form a C3-C30 saturated or unsaturated
 hydrocarbon ring,

X_3 , X_4 , X_5 , Y_3 , Y_4 , and Y_5 are each independently
 selected from the group consisting of a hydrogen atom, a
 15 C1-C30 alkyl group, a halogen group, a C1-C30 alkoxy
 group, a C6-C30 aryl group, a thiophenoxy group, a C1-C30
 thioalkoxy group, a C1-C20 alkoxycarbonylmethoxy group,
 and any combination thereof,

Z, which denotes an anion, is OSO_2CF_3 , $\text{OSO}_2\text{C}_4\text{F}_9$, $\text{OSO}_2\text{C}_8\text{F}_{17}$, $\text{N}(\text{CF}_3)_2$, $\text{N}(\text{C}_2\text{F}_5)_2$, $\text{N}(\text{C}_4\text{F}_9)_2$, $\text{C}(\text{CF}_3)_3$, $\text{C}(\text{C}_2\text{F}_5)_3$, $\text{C}(\text{C}_4\text{F}_9)_3$, or a functional group represented by Formula 22 below:

Formula 22



5

wherein V_1 and V_2 are each independently a halogen atom,

W_1 is $-(\text{C}=\text{O})-$ or $-(\text{SO}_2)-$,

W_2 is a C1-C10 alkanediyl group,

10 W_3 is selected from the group consisting of a C3-C30 cycloalkanediyl group, a C6-C30 arylene group, and a C5-C30 heterocycloalkylene group,

W_4 is selected from the group consisting of a hydrogen atom, a halogen group, a C1-C10 alkyl group, a
15 C2-C20 alkenyl group, a C1-C10 alkoxy group, a C1-C10 haloalkyl group, a (C1-C10 alkyl)thio group, a C3-C30 cycloalkyl group, a C6-C30 aryl group, a (C6-C30 aryl)oxy group, a (C6-C30 aryl)thio group, a C5-C30 heterocyclic group, and any combination thereof,

20 o is an integer of 0 to 1, and

p is an integer of 0 to 2.

16. The resist composition of claim 13, wherein the

amount of the acid generator is in the range of 0.3 to 10 parts by weight based on 100 parts by weight of solids of the resist composition.

5 17. The resist composition of claim 13, further comprising an additive selected from the group consisting of an alkali soluble quencher, an acid diffusion quencher, a surfactant, and any mixture thereof.

10 18. A method of forming a resist pattern, the method comprising:

 forming a resist film by coating the resist composition according to claim 13 on a substrate;

 heating the resist film, and exposing the resist film
15 to light to form a predetermined pattern; and

 developing the exposed pattern.

 19. The method of claim 18, wherein the exposing is performed using a light source selected from the group
20 consisting of a KrF excimer laser, an ArF excimer laser, an extreme ultraviolet laser, an X-ray, and an electron beam.