

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 is stripped off by a developer during a
10 development process to improve hydrophilicity of the surface of the resist film and allow the surface of the resist film to have a low static contact angle, so that a micropattern of the resist film with excellent sensitivity and high resolution can be formed, and a resist
15 composition including the additive.

Description of the Related Art

 With higher integration and higher speed of large scale integrated circuits (LSI) in recent years, accurate
20 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.

 However, as resolution improvement obtained by
25 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 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.

5 Prior Art

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

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

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

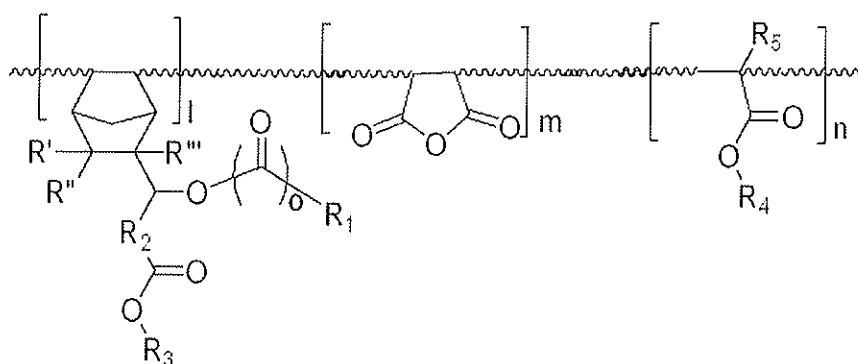
SUMMARY OF THE INVENTION

15 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
in water during an immersion lithography process and is
20 stripped off by a developer during a development process
to improve hydrophilicity of the surface of the resist
film and allow the surface of the resist film to have a
low static contact angle, so that a micropattern of the
resist film with excellent sensitivity and high resolution
25 can be formed.

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

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



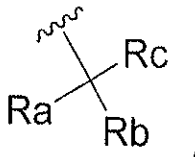
In Formula 1, R', R'' and R''' may be each independently selected from the group consisting of a hydrogen atom, a C1-C4 alkyl group, a halogen group, and a C1-C4 haloalkyl group in which one hydrogen atom is substituted with a halogen group.

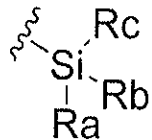
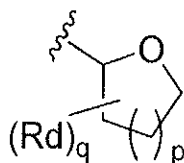
R₁ may be a hydrophobic group selected from the group consisting of a C1-C20 haloalkyl group, an organic silicon group, and a C3-C20 hydrocarbon group. If R₁ is an organic silicon group, o is 0, and if R₁ is a C1-C20 haloalkyl group or C3-C20 hydrocarbon group, o is 1.

R₂ 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 heterocycloalkenediyl group.

5 R_3 and R_4 may be each independently 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 may be fused
10
15 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.

R_5 may be a hydrogen atom or a C1-C8 alkyl group.

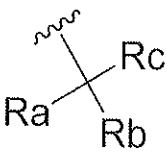
20 Here, l, m, and n are respectively numbers of the repeat units in a backbone, wherein $l+m+n=1$,

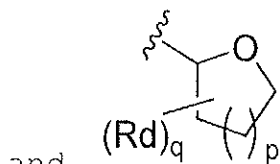
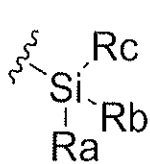
$0 < l/(1+m+n) < 0.99$, $0 < m/(1+m+n) \leq 0.20$, and $0 < n/(1+m+n) < 0.99$, and o may be an integer of 0 or 1.

In Formula 1, R_1 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.

In Formula 1, R_1 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.

In Formula 1, R_3 and R_4 may be each independently

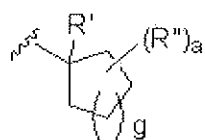
selected from the group consisting of ,



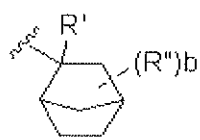
and R_a , R_b , R_c and R_d may be each independently selected from the group consisting of a C1-C10 alkyl group, a C3-C14 monocyclic cycloalkyl group, a C8-C20 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl group, a C10-C30 tetracyclic cycloalkyl group, a (C1-C5 alkyl)cycloalkyl group, a 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 may be 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.

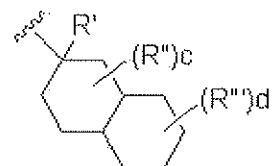
More preferably, R₃ and R₄ may be each independently selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxy-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups represented by Formulae 2a to 2k below.



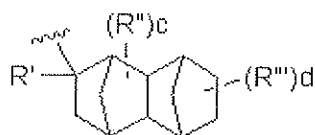
(2a)



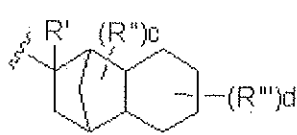
(2b)



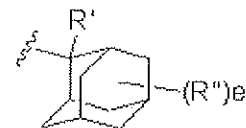
(2c)



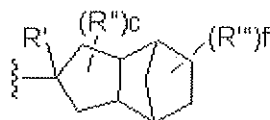
(2d)



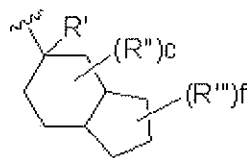
(2e)



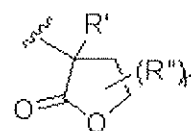
(2f)



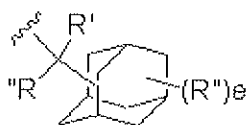
(2g)



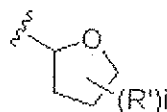
(2h)



(2i)



(2j)

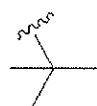


(2k)

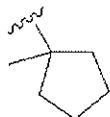
In Formulae 2a to 2k, R', R'' and R''' may be each independently a hydrogen atom or a C1-C10 alkyl group, a and e may be each independently an integer of 0 to 15, b may be an integer of 0 to 11, c and d may be each independently an integer of 0 to 9, f may be an integer of 0 to 7, g and i may be each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

In Formula 1, R₃ and R₄ may be each independently selected from the group consisting of Formulae 3a to 3h

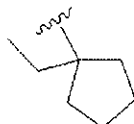
below.



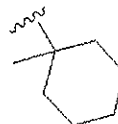
(3a)



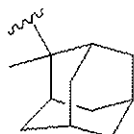
(3b)



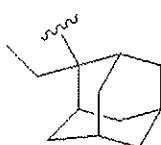
(3c)



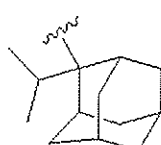
(3d)



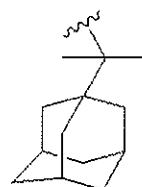
(3e)



(3f)



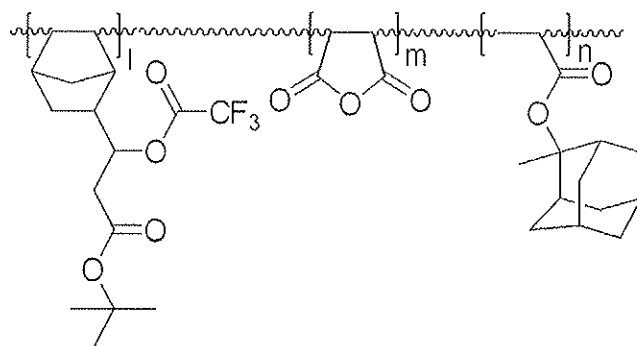
(3g)



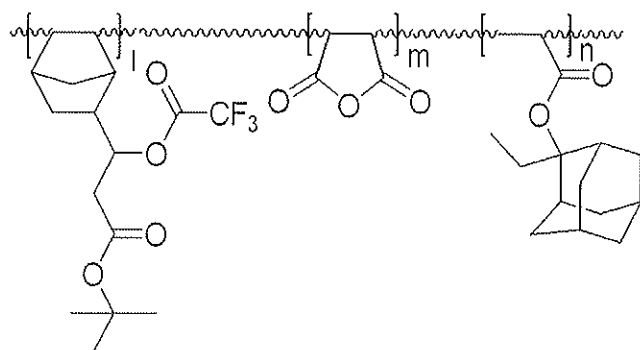
(3h)

The resist additive may be selected from the group
5 consisting of compounds represented by Formulae 4 to 11
below.

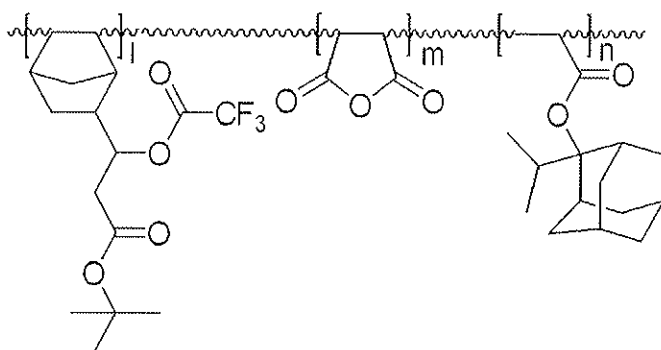
Formula 4



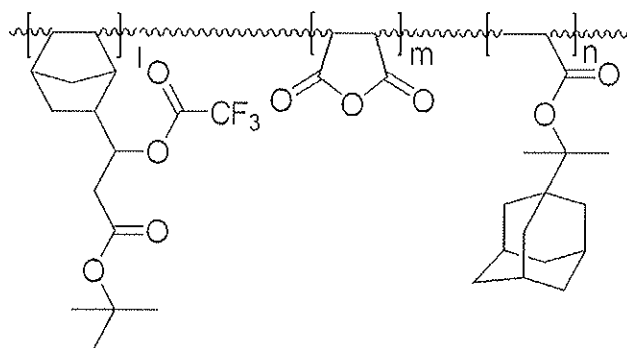
Formula 5



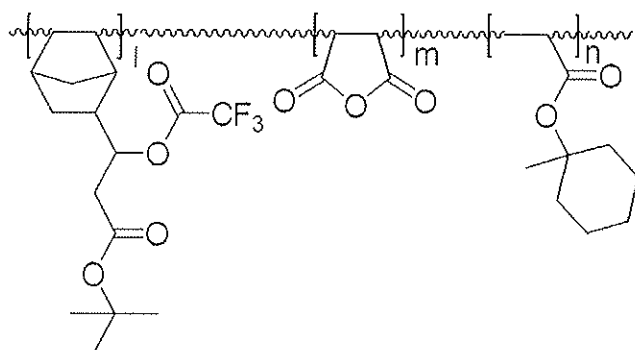
Formula 6



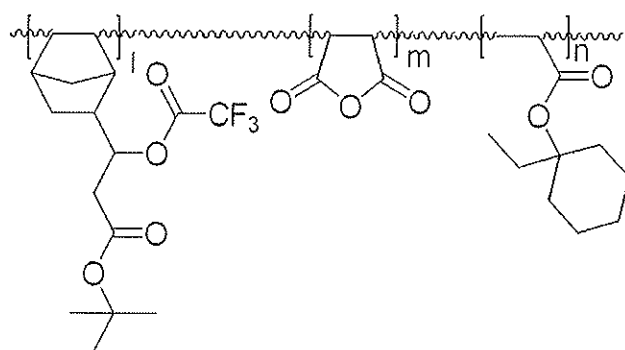
Formula 7



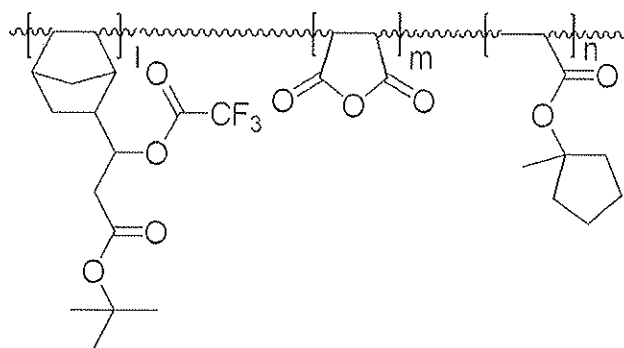
Formula 8



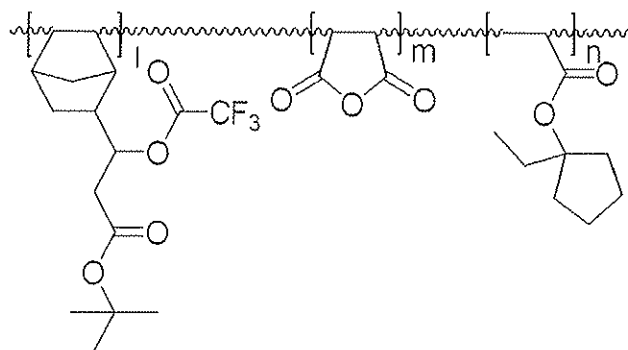
Formula 9



Formula 10



Formula 11



In Formulae 4 to 11, *l*, *m*, and *n* are respectively numbers of the repeat units in a backbone. Here, $l+m+n=1$, $0 < l/(l+m+n) < 0.99$, $0 < m/(l+m+n) \leq 0.2$, and $0 < n/(l+m+n) < 0.99$.

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

A polystyrene equivalent weight average molecular weight of the resist additive measured using gel
10 permeation chromatography may be in the range of 1,000 to 20,000 g/mol.

A ratio of weight average molecular weight/number average molecular weight of the resist additive may be in the range of 1 to 3.

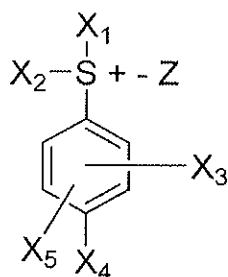
15 In accordance with an aspect of the present invention, the above and other objects can be accomplished by the provision of a resist composition including the resist additive, a resist base polymer, an acid generator, and a solvent.

20 The amount of the resist additive may be in the range

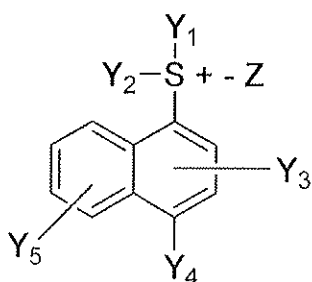
of 0.05 to 5% by weight based on the total weight of the resist composition.

The acid generator may include at least one compound selected from the group consisting of Formulae 14 and 15 below.

Formula 14



Formula 15

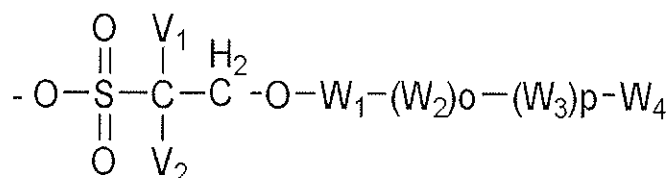


In Formulae 14 and 15, X₁, X₂, Y₁, and Y₂ may be each independently selected from the group consisting of a hydrogen atom, a C1-C10 alkyl group, an allyl group, a perfluoroalkyl group, a benzyl group, a C6-C30 aryl group, and any combination thereof. X₁ and X₂ may be fused to form a C3-C30 saturated or unsaturated hydrocarbon ring, and Y₁ and Y₂ may be fused to form a C3-C30 saturated or unsaturated hydrocarbon ring.

X₃, X₄, X₅, Y₃, Y₄, and Y₅ 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 alkoxycarbonylmethoxy group, and any combination thereof.

Z, which denotes an anion, may be OSO₂CF₃, OSO₂C₄F₉, OSO₂C₈F₁₇, N(CF₃)₂, N(C₂F₅)₂, N(C₄F₉)₂, C(CF₃)₃, C(C₂F₅)₃, C(C₄F₉)₃, or a functional group represented by Formula 16 below.

Formula 16



In Formula 16, V₁ and V₂ may be each independently a halogen atom, W₁ may be -(C=O)- or -(SO₂)-, W₂ may be a C1-C10 alkanediyl group, W₃ 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, W₄ 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, o may be an integer of 0 to 1, and p may be 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.

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

10 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 predetermined pattern, and developing the exposed pattern.

15 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.

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

DETAILED DESCRIPTION OF THE INVENTION

25 Hereinafter, the present invention will be described in detail. However, descriptions of these example embodiments are only provided for illustrative purposes, and

should not be construed as limiting the scope and spirit of the present invention. The following detailed description of the present invention is intended to provide further explanation of the invention as claimed.

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

10 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.

15 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.

20 The term 'cycloalkyl group' as used herein refers to a C3-C30 cycloalkyl group, unless otherwise stated, and includes monocyclic, dicyclic, tricyclic, and tetracyclic
25 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.

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 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 disclosed herein.

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

tetrahydroquinolinyl, tetrahydroisoquinolinyl,
decahydroquinolinyl, octahydroisoquinolinyl, azocinyl,
triazinyl, 6H-1,2,5-thiadiazinyl, 2H,6H-1,5,2-dithiazinyl,
thienyl, thianthrenyl, pyranyl, isobenzofuranyl, chromenyl,
5 xanthenyl, phenoxathinyl, 2H-pyrrolyl, isothiazolyl,
isoxazolyl, pyrazinyl, pyridazinyl, indoliziny, isoindolyl,
3H-indolyl, 1H-indazolyl, purinyl, 4H-quinoliziny,
phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl,
cinnolinyl, pteridinyl, 4aH-carbazolyl, carbazolyl, β -
10 carbolinyl, phenanthridinyl, acridinyl, pirimidinyl,
phenanthrolinyl, phenazinyl, phenothiazinyl, furazanyl,
phenoxazinyl, isochromanyl, chromanyl, imidazolidinyl,
imidazolinyl, pyrazolidinyl, pyrazolinyl, piperazinyl,
indolinyl, isoindolinyl, quinuclidinyl, morpholinyl,
15 oxazolidinyl, benzotriazolyl, benzisoxazolyl, oxindolyl,
benzoxazolinyl, isatinoyl, and bis-tetrahydrofuranly, which
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.

20 All compounds or substituents used herein may be
substituted or unsubstituted, unless stated otherwise. In
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
25 cyano group, a nitro group, an amino group, a thio group, a

methythio group, an alkoxy group, a nitrile group, an 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 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.

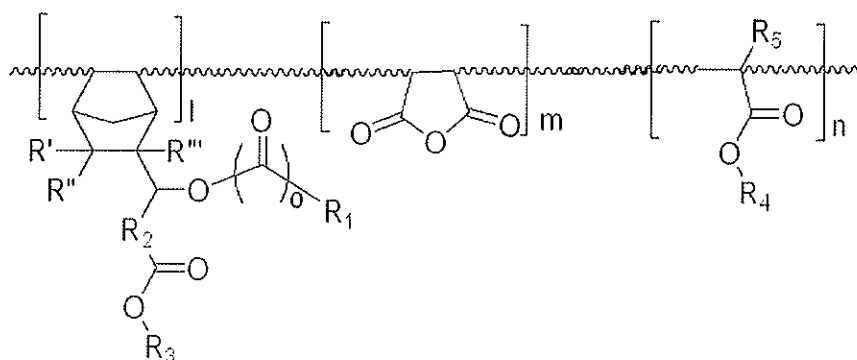
Conventionally, when a resist pattern is formed by ArF immersion lithography, acids or amine compounds contained in a resist film are dissolved in water between a projection lens and a wafer substrate, and accordingly the projection lens may be contaminated, the resist pattern may be deformed or collapse due to swelling, or various defects such as bubbles and watermarks may be generated.

According to the present invention, in liquid immersion lithography utilizing an ArF excimer laser having a wavelength of 193 nm as a light source and interposing water between a projection lens and a substrate, a resist additive including a norbornene monomer-derived repeat unit having a hydrophobic group is added to a resist composition to obtain the same effect as a protective film formed on the

resist film to protect resist materials. In addition, a maleic anhydride-derived repeat unit is added to the backbone of a copolymer obtained from the additive in an appropriate amount such that the hydrophobic group may be stripped off by a developer during a development process to provide hydrophilicity, thereby reducing defects on the surface of the resist film.

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

Formula 1



In Formula 1, R', R'' and R''' may be each independently selected from the group consisting of a hydrogen atom, a C1-C4 alkyl group, a halogen group and a C1-C4 haloalkyl group in which one hydrogen atom is substituted with a halogen group.

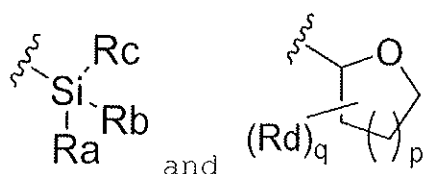
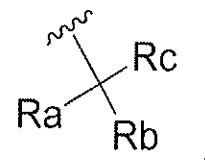
R₁ may be a hydrophobic group selected from the group consisting of a C1-C20 haloalkyl group, an organic silicon group, and a C3-C20 hydrocarbon group. If R₁ is an organic

silicon group, o is 0, and if R₁ is a C1-C20 haloalkyl group or a C3-C20 hydrocarbon group, o is 1.

R₂ 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 heterocycloalkenediyl group.

R₃ and R₄ may be each independently an acid labile

group selected from the group consisting of



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 may be 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.

R₅ may be a hydrogen atom or a C1-C8 alkyl group.

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

In addition, o is an integer of 0 or 1.

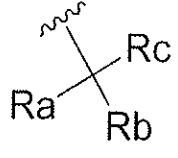
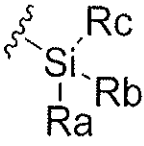
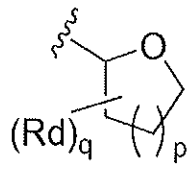
10 In Formula 1, R', R'' and R''' may be each independently selected from the group consisting of a hydrogen atom, a C1-C4 alkyl group, a fluoro group, and a C1-C4 fluoroalkyl in which one hydrogen atom is substituted with a fluoro group, preferably selected from the group consisting of a hydrogen atom, a methyl group, a fluoro group, and a trifluoromethyl group, more preferably a hydrogen atom.

15 In Formula 1, R₁ 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, 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.

20

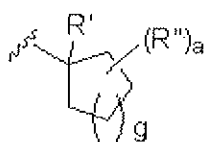
In Formula 1, R_2 may be selected from the group consisting of a C1-C10 alkanediyl group, a C2-C10 alkenediyl group, a C1-C10 heteroalkanediyl group, a C2-C10 heteroalkenediyl group, a C3-C18 cycloalkanediyl group, a C3-C18 cycloalkenediyl group, a C2-C18 heterocycloalkanediyl group, and a C3-C18 heterocycloalkanediyl group, preferably methylene, ethylidene, propylidene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, 2,2-dimethylpentamethylene, $-OCH_2-$, $-OCH(Cl)-$, $-CO-$, $-COCH_2-$, $-COCH_2CH_2-$, $-CH_2-O-CH_2-$, $-CH_2-O-CH_2CH_2-$, $-CH_2CH_2-O-CH_2-$, $-CH_2-O-CH_2CH_2CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-CH_2CH_2CH_2-O-CH_2-$, $-C(CH_3)_2CH_2-$, $-CH(CH_3)CH_2-$, $-CH(CH_2CH_3)-$, $-CH(OCH_3)-$, $-C(CF_3)(OCH_3)-$, $-CH_2-S-CH_2-$, $-CH_2-S-CH_2CH_2-$, $-CH_2CH_2-S-CH_2-$, $-CH_2-S-CH_2CH_2CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$, $-CH_2CH_2CH_2-S-CH_2-$, $-CH(CH_2)CH-$, $-C(CH_2CH_2)-$, $-CH_2CO-$, $-CH_2CH_2CO-$, $-CH(CH_3)CH_2CO-$, $-CH(OH)-$, $-C(OH)(CH_3)-$, $-CH(F)-$, $-CH(Br)-$, $-CH(Br)CH(Br)-$, $-CH=CH-$, $-CH_2CH=CH-$, $-CH=CHCH_2-$, $-CH=CHCO-$, $-C_7H_9-$, and $-C_{10}H_{14}-$.

In Formula 1, R_3 and R_4 may be each independently

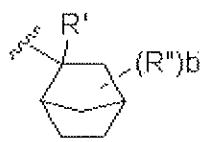
selected from the group consisting of , , and . In this regard, R_a , R_b , R_c and R_d may be each independently selected from the group consisting

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

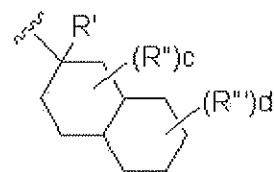
More preferably, R₃ and R₄ may be each independently selected from the group consisting of a t-butyl group, a trimethylsilyl group, a hydroxy-2-ethyl group, a 1-methoxypropyl group, a 1-methoxy-1-methylethyl group, a 1-ethoxypropyl group, a 1-ethoxy-1-methylethyl group, a 1-methoxy-1-ethyl group, a 1-ethoxy-1-ethyl group, a t-butoxy-2-ethyl group, a 1-isobutoxy-1-ethyl group, and groups
15 represented by Formulae 2a to 2k below.



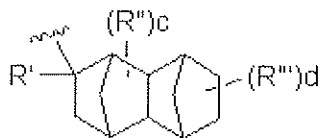
(2a)



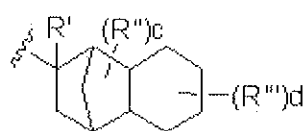
(2b)



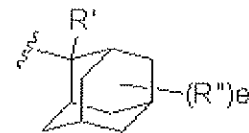
(2c)



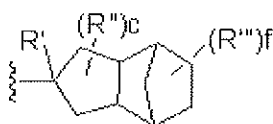
(2d)



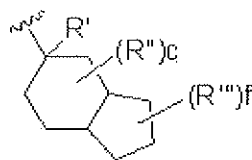
(2e)



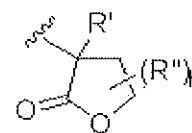
(2f)



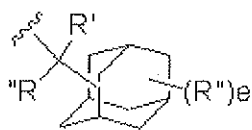
(2g)



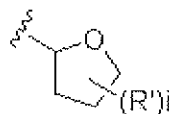
(2h)



(2i)



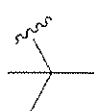
(2j)



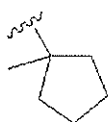
(2k)

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 $0 \leq c+f \leq 15$.

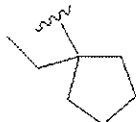
More preferably, R₃ and R₄ may be each independently selected from the group consisting of Formulae 3a to 3h below.



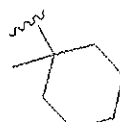
(3a)



(3b)



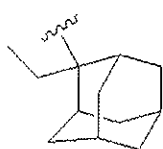
(3c)



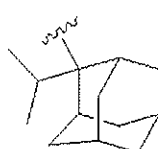
(3d)



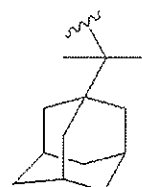
(3e)



(3f)



(3g)



(3h)

In Formula 1, R_5 may be a hydrogen atom or a C1-C4 alkyl group, more preferably, a hydrogen atom or a methyl group.

5 In general, in order to increase scan speed, a static contact angle (SCA) of a resist film needs to be greater than 90° . However, a high SCA may cause blob defects during development after exposure. Thus, blob defects may be reduced by reducing the SCA of the surface of the resist

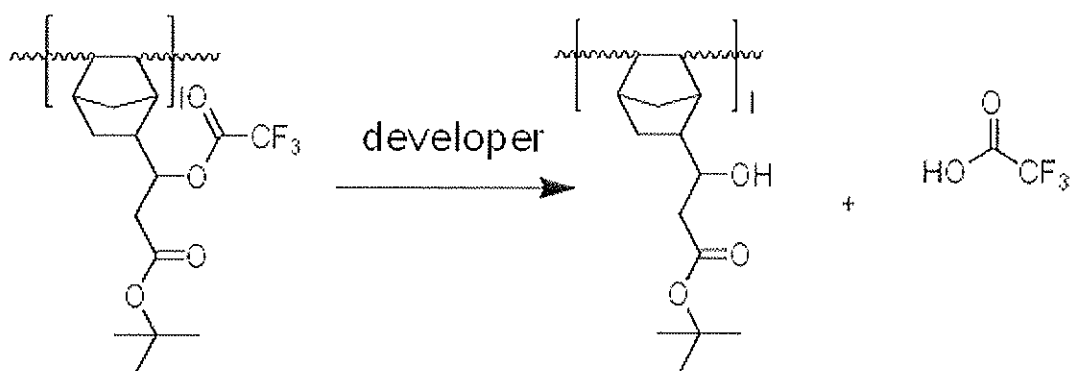
10 film. In this regard, in the copolymer according to the present invention, by optimizing the content of the maleic anhydride-derived repeat unit contained in the backbone, the hydrophobic group is stripped off by a developer, such as 2.38% by weight of trimethylammonium hydroxide (TMAH),

15 during development to be converted into a hydroxyl group and provide hydrophilicity to the copolymer. Thus, defects on the surface of the resist film may be reduced. The additive according to the present invention includes a hydrophobic

group having an electron withdrawing group, such as a trihaloacetyl group, substituted at an α -carbon. Thus, the additive may improve hydrophobicity of the resist film to prevent materials of the resist films from being leached during liquid immersion lithography.

Particularly, in the resist additive copolymer according to the present invention, the hydrophobic group contained in the norbornene-derived repeat unit 1 improves hydrophobicity of the surface of the resist film during exposure to prevent the leaching in water during lithography and stripping off by the developer at exposed regions during development to be converted into a hydroxyl group as shown in Reaction Scheme 1 below. Thus, the copolymer has hydrophilicity, and the surface of the resist film has a low SCA, thereby reducing blob defects. In addition, an acid labile group, such as a t-butyl group, attached to one end of the norbornene-derived repeat unit 1 is converted from a hydrophobic group to a hydrophilic group via acid-induced deprotection reaction at the exposed regions. As a result, the additive is easily washed by the developer. However, Reaction Scheme 1 below is exemplary, and the present invention is not limited thereto.

Reaction Scheme 1



In the copolymer, the maleic anhydride-derived repeat unit *m* is ring-opened by the developer at non-exposed regions to form carboxyl groups as shown in Reaction Scheme 2 below. Thus, hydrophilicity on the surface thereof is improved. 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 2 below is exemplary, and the present invention is not limited thereto.

Reaction Scheme 2



In addition, the copolymer according to the present invention includes an acryl-derived repeat unit *n* having an acid labile functional group. The acid labile functional group is deprotected during exposure to be converted from a hydrophobic group to a hydrophilic group. As a result, the

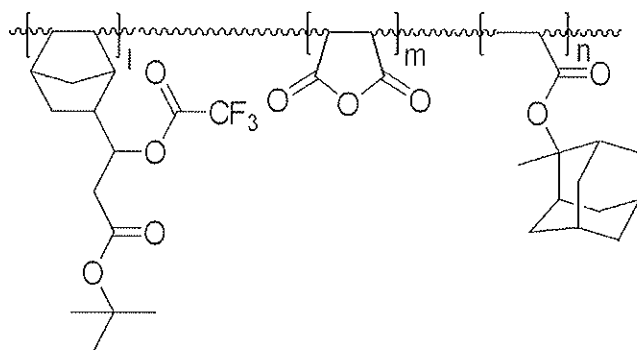
acid labile functional group is easily removed during development at the exposed regions.

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 $0<l/(l+m+n)<0.9$, $0<m/(l+m+n)\leq 0.2$, and $0<n/(l+m+n)<0.9$. When the repeat units satisfy the above conditions, the resist film may have hydrophobicity during the liquid immersion lithography. Particularly, when the content of the maleic anhydride-derived repeat unit m is less than 20 mol%, a CA value may be reduced, thereby reducing defects. If the content of the maleic anhydride-derived repeat unit m is greater than 20 mol%, the hydrophobic group may be dissolved by the developer at the non-exposed regions. More preferably, the content of the maleic anhydride-derived repeat unit m may be in the range of 5 to 15 mol%.

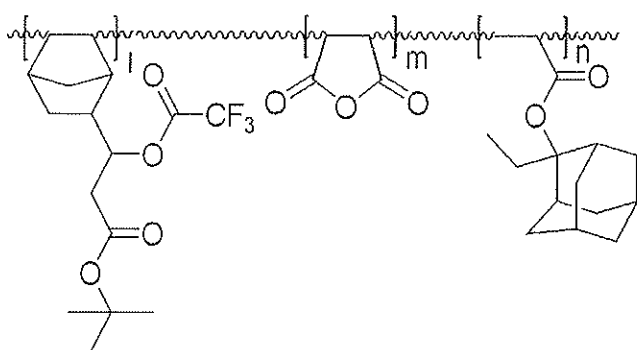
The resist additive according to the present invention having the structure shown above may be a block copolymer, a random copolymer, or a graft copolymer.

Examples of the resist additive may include compounds represented by Formulae 4 to 11 below. In the structural formulae, the order of the repeat units may be modified.

Formula 4

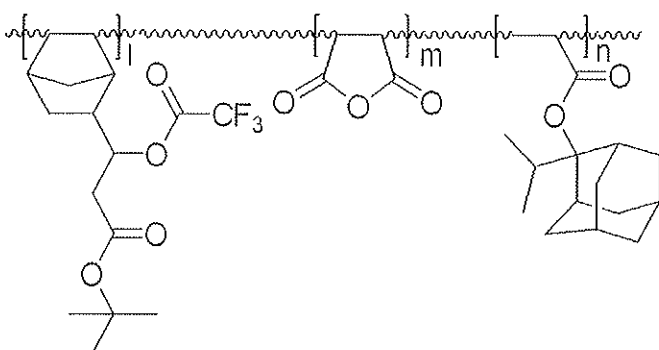


Formula 5

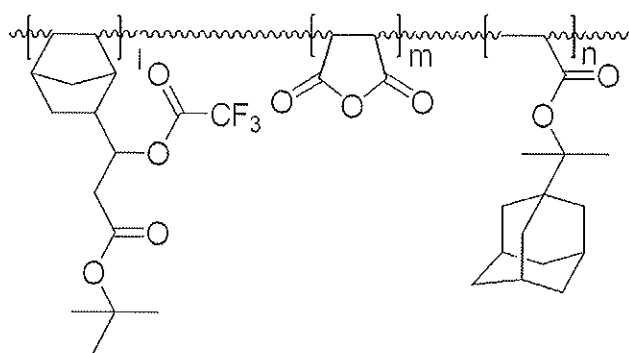


5

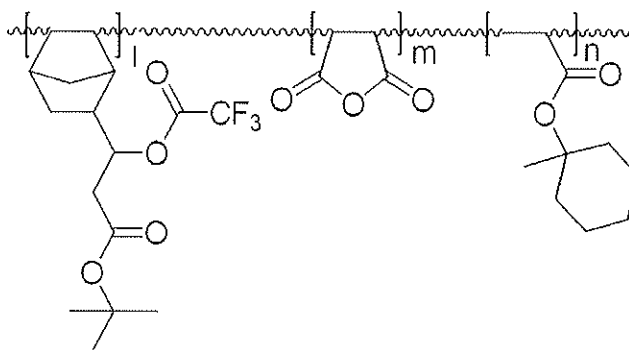
Formula 6



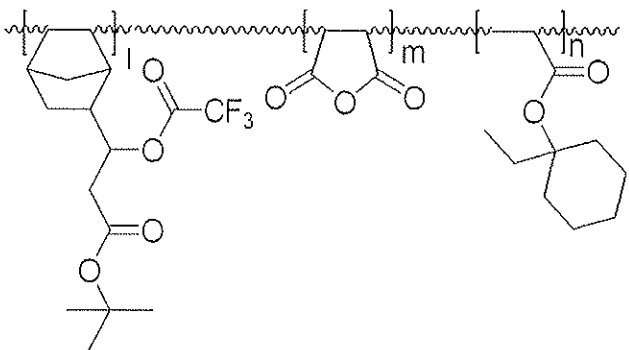
Formula 7



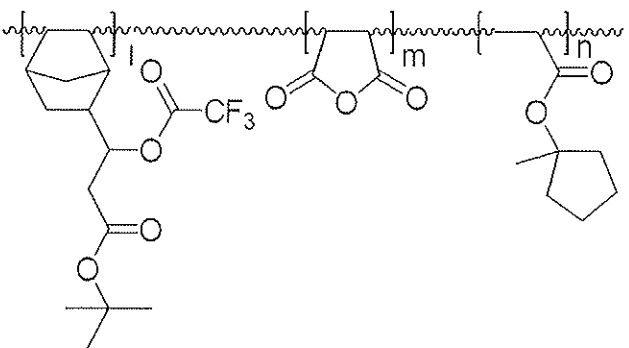
Formula 8



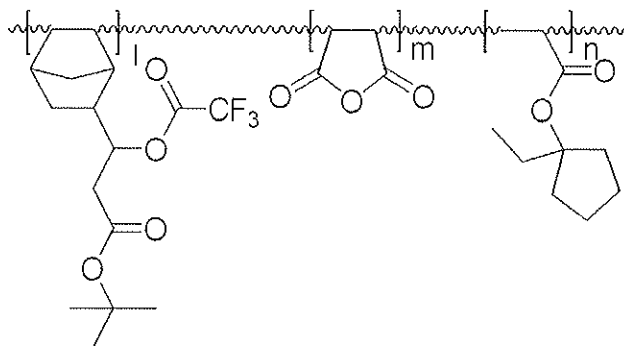
Formula 9



Formula 10



Formula 11



In Formulae 4 to 11, l , m , and n are respectively numbers of the repeat units in the backbone. Here, $l+m+n=1$,
 5 $0 < l/(l+m+n) < 0.99$, $0 < m/(l+m+n) \leq 0.20$, and $0 < n/(l+m+n) < 0.99$.

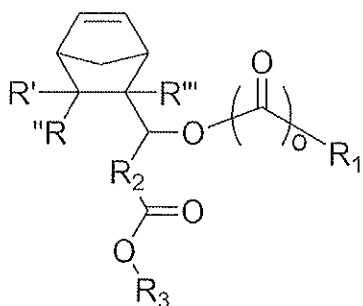
The resist additive according to the present invention may have a polystyrene equivalent weight average molecular weight (M_w) measured using gel permeation chromatography (GPC) in the range of 1,000 to 20,000 g/mol. If the M_w of
 10 the copolymer is too low, intermixing may occur or elution by pure water may occur during immersion lithography. On the other hand, if the M_w of the copolymer is too high, the film may not be appropriately formed or alkali solubility may be reduced. Preferably, the M_w of the copolymer may be
 15 in the range of 2,000 to 10,000 g/mol to have excellent solubility in the developer without being eluted in pure water.

In addition, the resist additive may have a molecular weight distribution, which is a weight average molecular weight/number average molecular weight (M_w/M_n) ratio, in the
 20

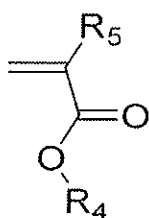
range of 1 to 3, more preferably 1 to 2. If the molecular weight distribution is greater than 3, line edge roughness characteristics may be deteriorated. Thus, a resist additive having Mw and molecular weight distribution within the ranges described above is used as a photoresist composition providing excellent developing properties, coating properties, and thermal resistance.

The resist additive according to the present invention having the above-mentioned structure may be prepared using a norbornene derivative represented by Formula 12 below, a maleic anhydride monomer, and an acryl monomer represented by Formula 13 below by known polymerization, such as bulk polymerization, solution polymerization, suspension polymerization, bulk and suspension polymerization, and emulsion polymerization.

Formula 12



Formula 13



In Formulae 12 and 13, R', R'', R''', R₁ to R₅ 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 resist additive 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 a resist base polymer, an acid generator, and a solvent in addition to the resist additive.

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 less than 0.05% by weight, the effect of the additive is negligible. On the other hand, if the amount of the resist additive is greater than 5% by weight, watermarks may be generated due to high CA.

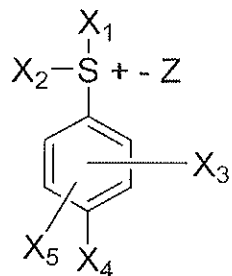
The resist base polymer may be any polymer used as a base resin in the formation of the resist film without limitation. Examples of the resist base polymer may include (meth)acrylic acid ester polymers, (α -trifluoromethyl)acrylic acid ester-maleic anhydride

copolymer, cycloolefin-maleic anhydride copolymers, polynorbornene, cycloolefin ring-opening metathesis (ROMP) polymerization polymers, hydrogenated cycloolefin ROMP polymers, copolymers of hydroxystyrene with one selected
5 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.

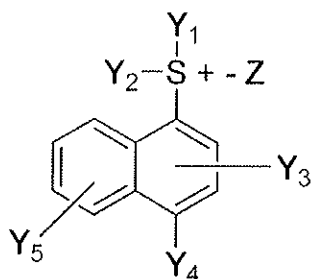
10 The base polymer may be contained in the resist composition in an amount in the range of 3 to 20% by weight. If the amount of the base polymer is less than 3% by weight, a film with a desired thickness may not be formed due to too low viscosity of the composition and a pattern loss may be
15 increased 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.

20 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 14 and 15, more preferably,
25 triphenylsulfonium nonaflate.

Formula 14



Formula 15



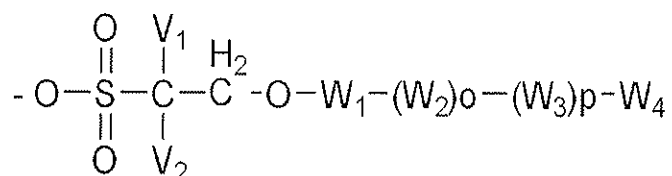
5 In Formulae 14 and 15, X_1 , X_2 , Y_1 and Y_2 may be each independently selected from the group consisting of a hydrogen atom, a C1-C10 alkyl group, an allyl group, a C1-C10 perfluoroalkyl group, a benzyl group, a C6-C30 aryl group, and any combination thereof. X_1 and X_2 may be fused
10 to form 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
15 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 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 16 below.

Formula 16

5



In Formula 16, V_1 and V_2 may be each independently a halogen atom.

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

10

W_2 may be a C1-C10 alkanediyl group.

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

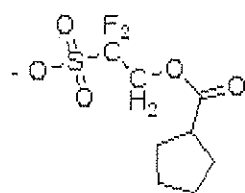
Here, o may be an integer of 0 to 1.

Here, p may be an integer of 0 to 2.

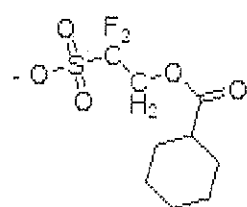
In the acid generator, a diffusion length of acid in a resist film may be appropriately maintained short and the

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.

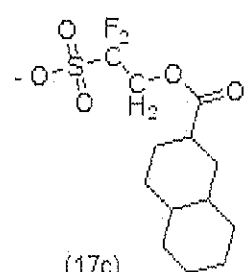
5 Preferably, Z, which denotes an anion, in Formula 16 may be selected from the group consisting of functional groups represented by Formulae 17a to 17l and 18a to 18x below.



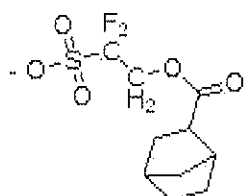
(17a)



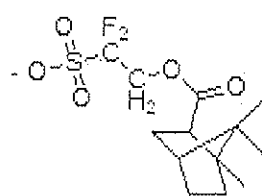
(17b)



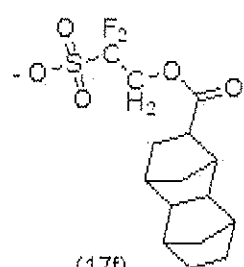
(17c)



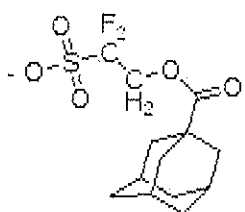
(17d)



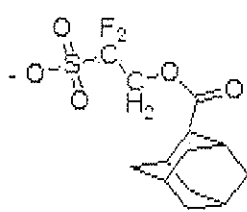
(17e)



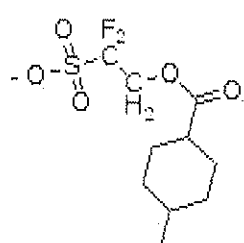
(17f)



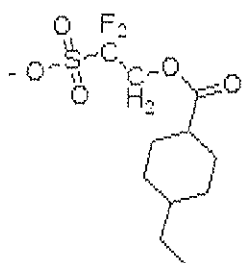
(17g)



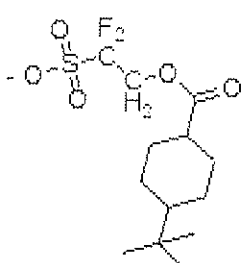
(17h)



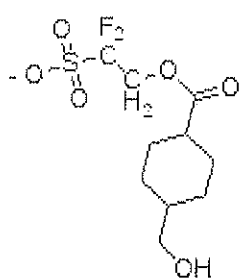
(17i)



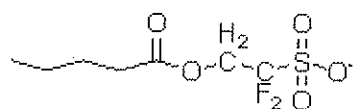
(17j)



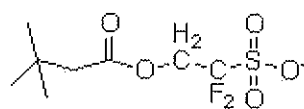
(17k)



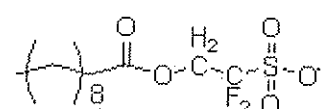
(17l)



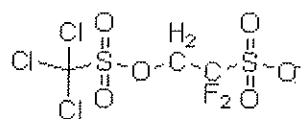
(18a)



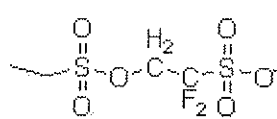
(18b)



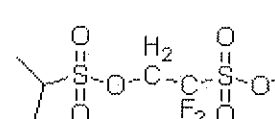
(18c)



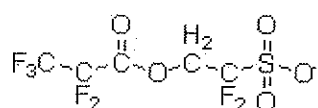
(18d)



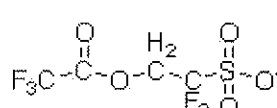
(18e)



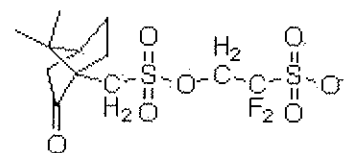
(18f)



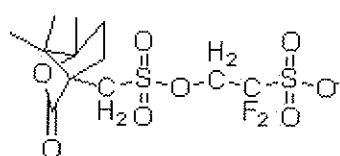
(18g)



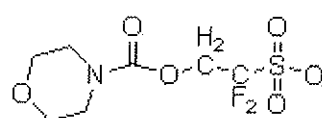
(18h)



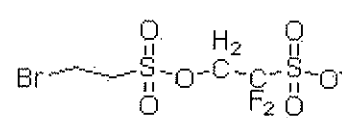
(18i)



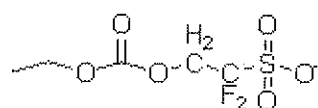
(18j)



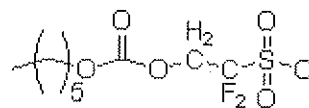
(18k)



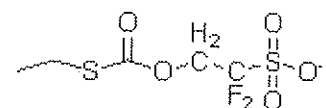
(18l)



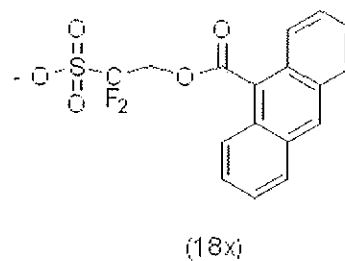
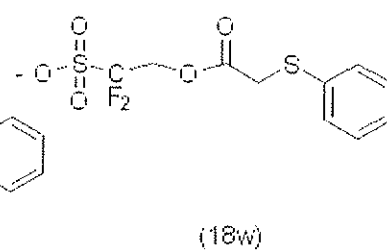
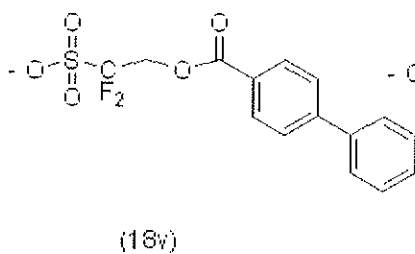
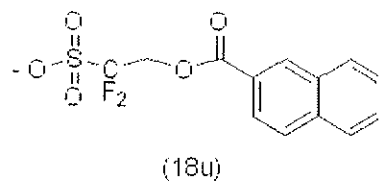
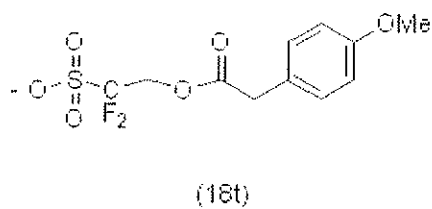
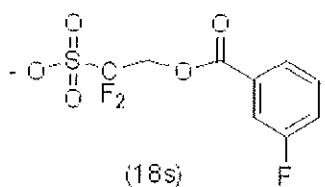
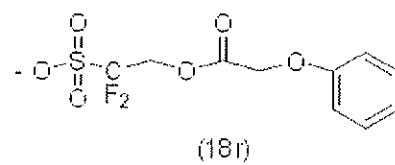
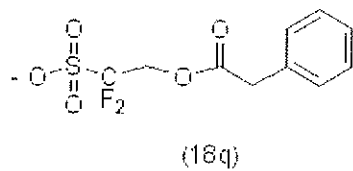
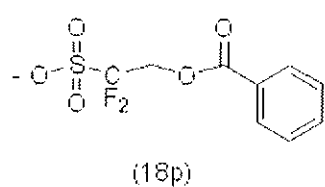
(18m)



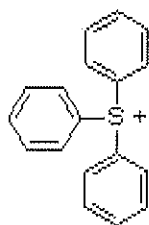
(18n)



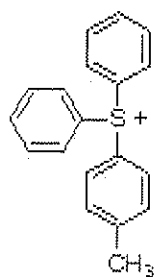
(18o)



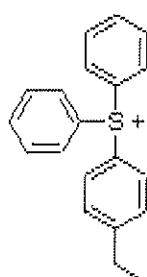
In addition, in Formulae 14 and 15, a cationic portion may be represented by Formulae 19a to 19p below.



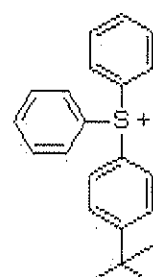
(19a)



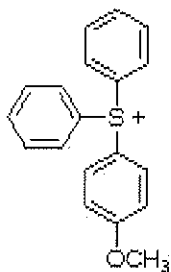
(19b)



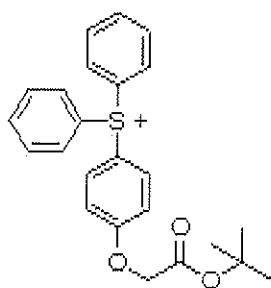
(19c)



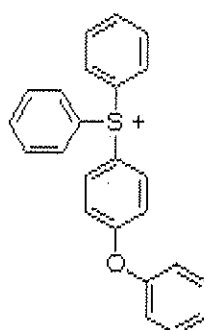
(19d)



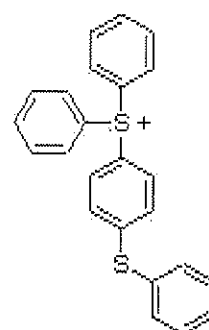
(19e)



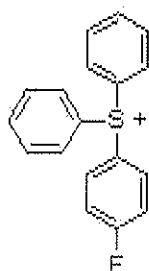
(19f)



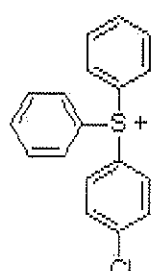
(19g)



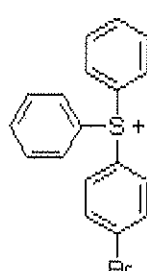
(19h)



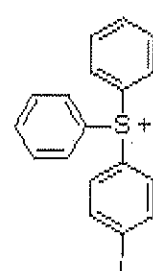
(19i)



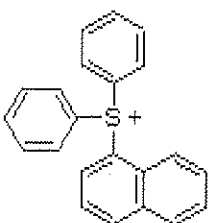
(19j)



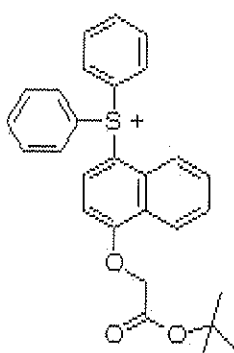
(19k)



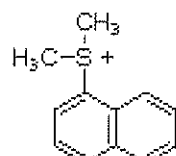
(19l)



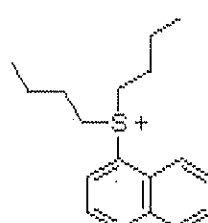
(19m)



(19n)



(19o)



(19p)

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.

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

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, and a surfactant, and the additives may be used alone or in combination of at least two thereof.

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.

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, N,N,N',N'-
 5 tetramethyltetraethylenepentamine, dimethylethylamine,
 methylethylpropylamine, benzylamine, phenethylamine,
 benzyldimethylamine, tetramethyl ammonium hydroxide, aniline,
 N,N-dimethyltoluidine, triphenylamine, phenylenediamine,
 pyrrole, oxazole, isooxazole, thiazole, isothiazole,
 10 imidazole, pyrazole, pyrroline, pyrrolidine, imidazoline
 derivatives, imidazolidine derivatives, pyridine derivatives,
 pyridazine derivatives, pyrimidine derivatives, pyrazine
 derivatives, pyrazoline derivatives, pyrazolidine
 derivatives, piperidine derivatives, piperazine derivatives,
 15 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-
 20 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,
 25 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 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 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 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 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 rays such 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/cm², preferably about 10 to about 100 mJ/cm². 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.

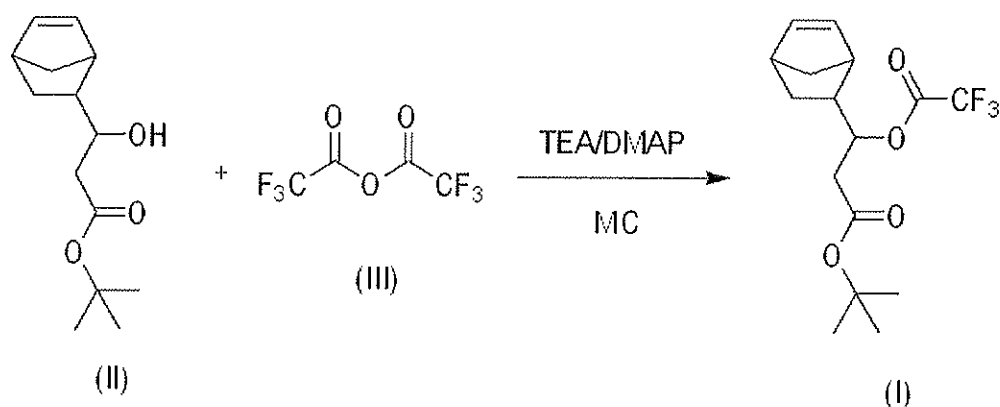
Hereinafter, the present invention will be described more fully with reference to the following examples.

However, the following examples are capable of being embodied through modifications and alternative forms, and there is no intent to limit the embodiments to the particular forms disclosed herein.

Preparation Example: Synthesis of Monomer and Polymer

Monomer Synthesis Example 1

Synthesis of 3-bicyclo[2.2.1]hept-5-en-2-yl-3-(2,2,2-trifluoro-acetoxy)-propionic acid tert-butyl ester (BHP-5) monomer



46.71 g of triethylamine was slowly added to a solution prepared by dissolving 100 g of 3-bicyclo[2,2,1]hept-5-en-2-yl-3-hydroxypropionic acid tert-butyl ester (BHP) II, 105.75 g of trifluoroacetic anhydride III, and 4.67 g of dimethyl-pyridine-4-yl-amine in 1 L of methylene chloride at 0°C, and the mixture was stirred at room temperature for 3 hours. The resultant was dissolved in 500 ml of methylene chloride, washed with acid and distilled water, and then an organic layer was separated. A

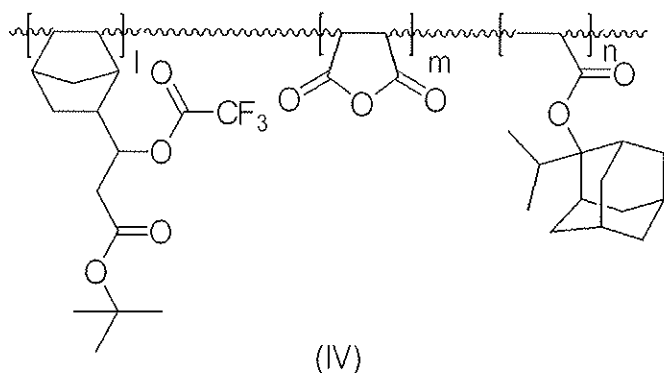
solvent was removed from the separated organic layer to obtain 130 g of BHP-5 (Compound I) as an intermediate.

¹H-NMR: (ppm) 0.6(d, 1H), 0.82(d, 1H), 1.25(m, 1H), 1.42(m, 1H), 1.58(s, 1H), 1.7(m, 1H), 1.9(m, 1H), 2.08(m, 12H), 2.15~2.6(m, 3H) 2.88(m, 2H), 4.7(m, 1H), 5.15(m, 1H), 5.25(m, 1H), 5.9(s, 1H), 6.22(s, 1H)

Polymer Synthesis Example 1

15 g of BHP-5 prepared in Monomer Synthesis Example 1, as a monomer for polymerization, 1.24 g of dimethyl azobisobutyrate, and 12 g of 1,4-dioxane were added to a flask and mixed. The air in the flask is replaced with nitrogen gas, and the flask was heated until temperature in the flask reached 75°. When the temperature in the flask was 75°, a solution prepared by dissolving 2 g of maleic anhydride and 7 g of 2-methyl-acrylic acid 2-isopropyladamantan-2-yl ester in 12 g of 1,4-dioxane was slowly added to the flask over 2 hours using a syringe pump. Then, polymerization was further performed at the same temperature for 3 hours and terminated. The resultant reaction solution was cooled to room temperature. The cooled reaction solution was precipitated using an excess of n-hexane, and the precipitates were filtered. The filtrate was dried at reduced pressure to obtain 12 g of Polymer IV represented by the following structural formula. A polystyrene equivalent

weight average molecular weight (Mw) was 6577 g/mol, and a weight average molecular weight/number average molecular weight (Mw/Mn) ratio was 1.6.

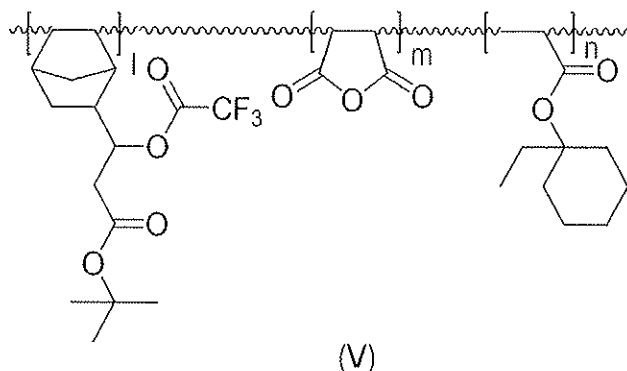


Polymer Synthesis Example 2

15 g of BHP-5 prepared in Monomer Synthesis Example 1, as a monomer for polymerization, 1.24 g of dimethyl azobisisobutylrate, and 12 g of 1,4-dioxane were added to a flask and mixed. The air in the flask is replaced with nitrogen gas, and the flask was heated until temperature in the flask reached 75°. When the temperature in the flask was 75°, a solution prepared by dissolving 2 g of maleic anhydride and 5 g of 1-ethyl-1-(1-methylene-allyloxy)-cyclohexane) in 12 g of 1,4-dioxane was slowly added to the flask over 2 hours using a syringe pump. Then, polymerization was further performed at the same temperature for 3 hours and terminated. The resultant reaction solution was cooled to room temperature. The cooled reaction

solution was precipitated using an excess of n-hexane, and the precipitates were filtered. The filtrate was dried at reduced pressure to obtain 13 g of Polymer V represented by the following structural formula. A polystyrene equivalent

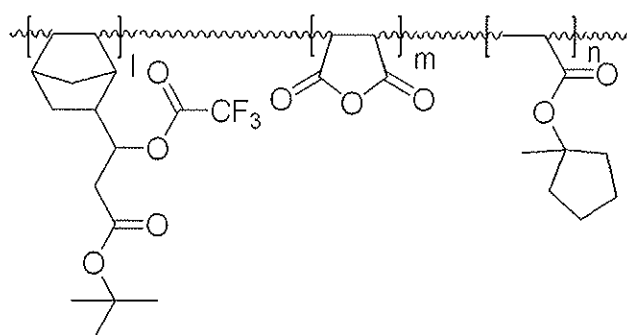
5 Mw was 4500 g/mol, and an Mw/Mn ratio was 1.5.



Polymer Synthesis Example 3

15 g of BHP-5 prepared in Monomer Synthesis Example 1, as a monomer for polymerization, 1.24 g of dimethyl azobisobutylrate, and 12 g of 1,4-dioxane were added to a flask and mixed. The air in the flask is replaced with nitrogen gas, and the flask was heated until temperature in the flask reached 75°. When the temperature in the flask was 75°, a solution prepared by dissolving 2 g of maleic anhydride and 6 g of 1-methyl-1-(1-methylenecyclohexyloxy)cyclopentane in 12 g of 1,4-dioxane was slowly added to the flask over 2 hours using a syringe pump. Then, polymerization was further performed at the same temperature for 3 hours and terminated. The resultant reaction solution

was cooled to room temperature. The cooled reaction solution was precipitated using an excess of n-hexane, and the precipitates were filtered. The filtrate was dried at reduced pressure to obtain 11 g of Polymer VI represented by the following structural formula. A polystyrene equivalent Mw was 5000 g/mol, and an Mw/Mn ratio was 1.6.

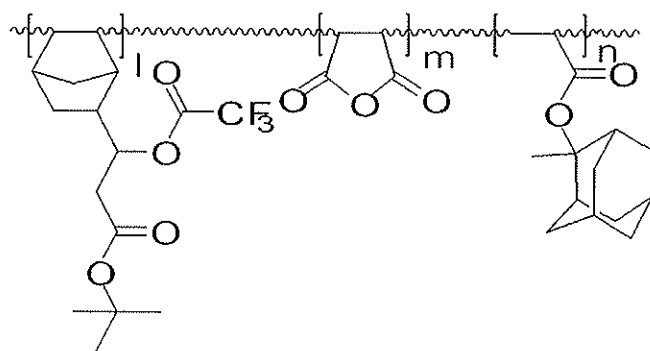


(VI)

Polymer Synthesis Example 4

15 g of BHP-5 prepared in Monomer Synthesis Example 1, as a monomer for polymerization, 1.24 g of dimethyl azobisobutyrate, and 12 g of 1,4-dioxane were added to a flask and mixed. The air in the flask is replaced with nitrogen gas, and the flask was heated until temperature in the flask reached 75°. When the temperature in the flask was 75°, a solution prepared by dissolving 2 g of maleic anhydride and 6 g of acrylic acid 2-methyl-adamantan-2-yl ester in 12 g of 1,4-dioxane was slowly added to the flask over 2 hours using a syringe pump. Then, polymerization was

further performed at the same temperature for 3 hours and terminated. The resultant reaction solution was cooled to room temperature. The cooled reaction solution was precipitated using an excess of n-hexane, and the precipitates were filtered. The filtrate was dried at reduced pressure to obtain 12 g of Polymer VII represented by the following structural formula. A polystyrene equivalent Mw was 6200 g/mol, and an Mw/Mn ratio was 1.63.

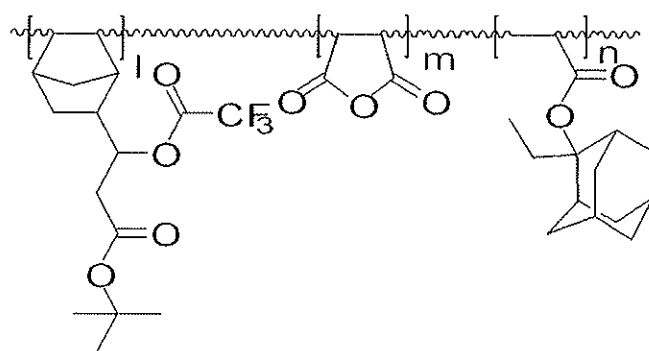


(VII)

Polymer Synthesis Example 5

15 g of BHP-5 prepared in Monomer Synthesis Example 1, as a monomer for polymerization, 1.24 g of dimethyl azobisobutyrate, and 12 g of 1,4-dioxane were added to a flask and mixed. The air in the flask is replaced with nitrogen gas, and the flask was heated until temperature in the flask reached 75°. When the temperature in the flask was 75°, a solution prepared by dissolving 2 g of maleic anhydride and 6.5 g of acrylic acid 2-ethyl-adamantan-2-yl

ester in 12 g of 1,4-dioxane was slowly added to the flask over 2 hours using a syringe pump. Then, polymerization was further performed at the same temperature for 3 hours and terminated. The resultant reaction solution was cooled to room temperature. The cooled reaction solution was precipitated using an excess of n-hexane, and the precipitates were filtered. The filtrate was dried at reduced pressure to obtain 13 g of Polymer VIII represented by the following structural formula. A polystyrene equivalent Mw was 5930 g/mol, and an Mw/Mn ratio was 1.55.

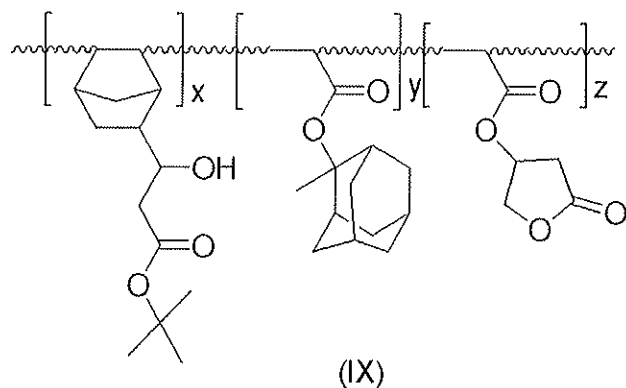


(VIII)

Evaluation Example 1: Evaluation of Hydrophobicity of Additive

1.0 g of each of the polymers synthesized in Polymer Synthesis Examples 1 to 5 was dissolved in 25 g of 4-methyl pentanol, and the solution was filtered using a 0.2 μ m polypropylene filter to prepare resist protective film compositions. For comparison with the additive according to the present invention in terms of effect, Polymer IX

represented by the following formula (Mw: 7,900 g/mol, Mw/Mn: 1.73, and a molar ratio of the repeat units: x:y:z=1:1:1) 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° 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 μ l 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

	Type of polymer as	Sliding angle before	Receding contact angle	Sliding angle after	Receding contact angle
--	--------------------	----------------------	------------------------	---------------------	------------------------

	resist additive	development (°)	before development(°)	development (°)	after development(°)
Synthesis Example 1	Polymer IV	93.7	78.6	74.2	42.
Synthesis Example 2	Polymer V	95.1	79.9	75.8	44.2
Synthesis Example 3	Polymer VI	94.5	79.5	72.6	43.7
Synthesis Example 4	Polymer VII	92.6	78.1	71.4	41.3
Synthesis Example 5	Polymer VIII	93.5	79.1	72.7	42.6
Comparative Example 1	Polymer IX	88.5	67.8	84.2	64.2

Referring to Table 1, the resist protective films including the polymers prepared in Polymer Synthesis Examples 1 to 5 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 5 were not negatively influenced.

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

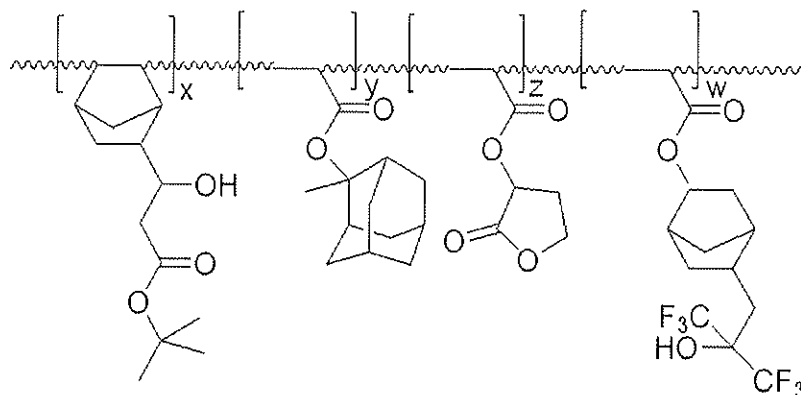
Examples 1 to 5

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,

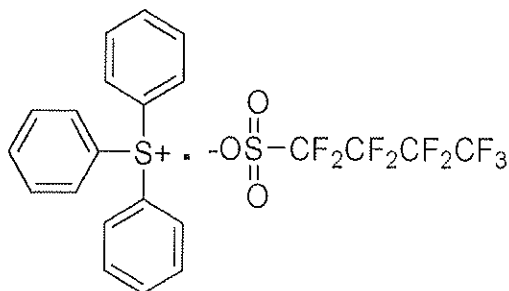
and 0.07 g of triisopropanol amine, as a quencher, were added to 80 g of propylene glycol monoethyl ether acetate (PGMEA), and the solution was filtered using a 0.2 μm polypropylene filter to form photoresist film compositions.

5

Formula 20



Formula 21



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 $^{\circ}$ for 60 seconds to form a photoresist film with a thickness of 120 nm.

15

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 5 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)	65 nm pattern foam
Example 1	Polymer IV	35.7	no standing wave
Example 2	Polymer V	43.5	no standing wave
Example 3	Polymer VI	52.4	no standing wave
Example 4	Polymer VII	52.7	no standing wave
Example 5	Polymer VIII	48.5	no standing wave
Comparative Example 2	-	49.2	serious roughness

Referring to Table 2, when a resist film was formed of a resist composition not including the resist additive 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 if the polymers prepared in Synthesis Examples 1 to 5 were used as resist additives.

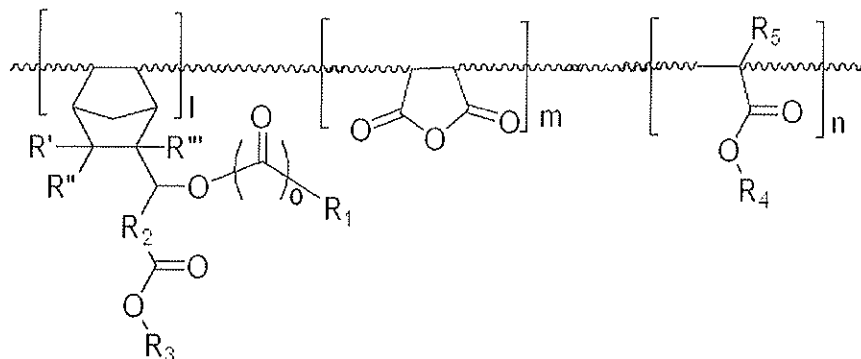
As is apparent from the above description, the present invention provides a resist additive which improves hydrophobicity of the surface of a resist film to prevent materials from being leached from the resist film in water during an immersion lithography process and is stripped off by a developer during a development process to improve hydrophilicity of the surface of the resist film and allow the surface of the resist film to have a low static contact angle, so that a micropattern of the resist film with excellent sensitivity and high resolution may be formed.

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

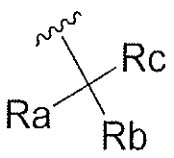


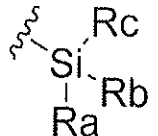
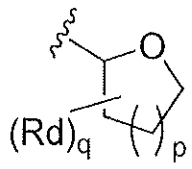
wherein R', R'' and R''' are each independently selected from the group consisting of a hydrogen atom, a C1-C4 alkyl group, a halogen group, and a C1-C4 haloalkyl group in which one hydrogen atom is substituted with a halogen group,

R₁ is a hydrophobic group selected from the group consisting of a C1-C20 haloalkyl group, an organic silicon group, and a C3-C20 hydrocarbon group, wherein if R₁ is an organic silicon group, o is 0, and if R₁ is a C1-C20 haloalkyl group or C3-C20 hydrocarbon group, o is 1,

R₂ 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 heterocycloalkenediyl group,

R₃ and R₄ are each independently 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
 5 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,
 10 and a C3-C30 heterocycloalkyl group or are 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,

R₅ is a hydrogen atom or a C1-C8 alkyl group,

15 1, m, and n are respectively numbers of the repeat
 units in a backbone, wherein 1+m+n=1, 0<1/(1+m+n)<0.99,
 0<m/(1+m+n)≤0.20, and 0<n/(1+m+n)<0.99, and

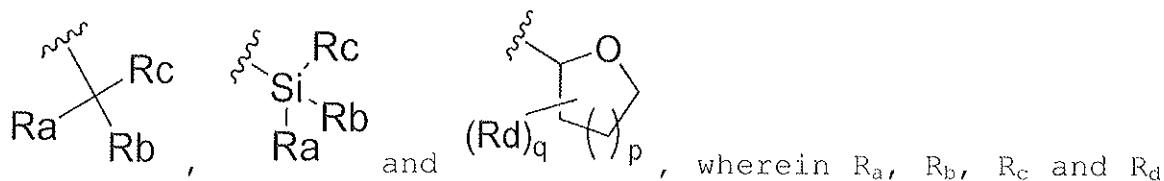
o is an integer of 0 or 1.

20 2. The resist additive of claim 1, wherein R₁ is
 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.

3. The resist additive of claim 1, wherein R_1 is 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.

4. The resist additive of claim 1, wherein R_3 and R_4 are each independently selected from the group consisting of



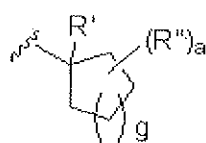
are each independently selected from the group consisting of a C1-C10 alkyl group, a C3-C14 monocyclic cycloalkyl group, a C8-C20 dicyclic cycloalkyl group, a C10-C30 tricyclic cycloalkyl group, a C10-C30 tetracyclic cycloalkyl group, a (C1-C5 alkyl)cycloalkyl group, a hydroxyalkyl group, a C1-C10 alkoxy 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 are 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.

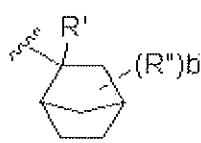
5

5. The resist additive of claim 1, wherein R₃ and R₄ are each independently 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 selected from the group consisting of Formulae 2a to 2k below:

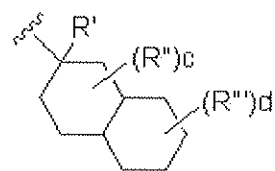
10



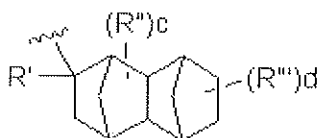
(2a)



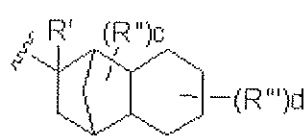
(2b)



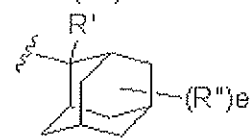
(2c)



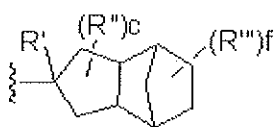
(2d)



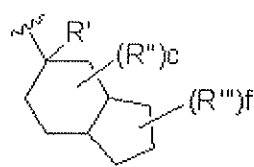
(2e)



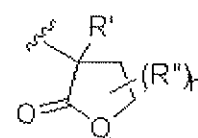
(2f)



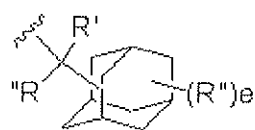
(2g)



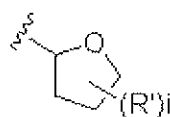
(2h)



(2i)



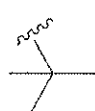
(2j)



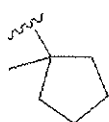
(2k)

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 $0 \leq c+f \leq 15$.

6. The resist additive of claim 1, wherein R_3 and R_4 are each independently selected from the group consisting of Formulae 3a to 3h below:



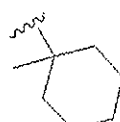
(3a)



(3b)



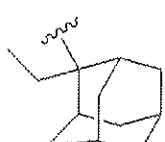
(3c)



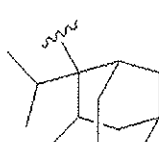
(3d)



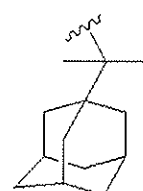
(3e)



(3f)



(3g)

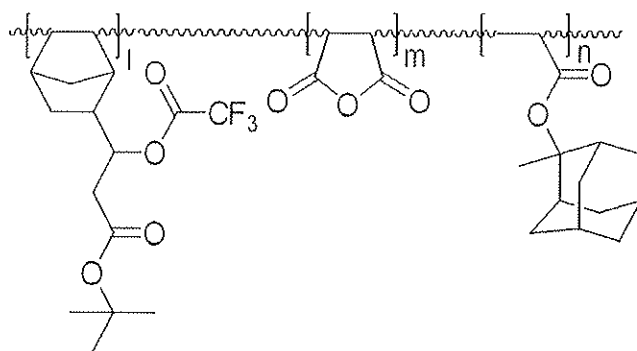


(3h)

5

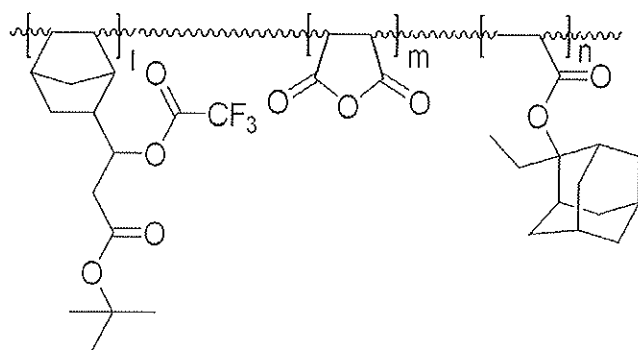
7. The resist additive of claim 1, wherein the resist additive is selected from the group consisting of compounds represented by Formulae 4 to 11 below:

Formula 4

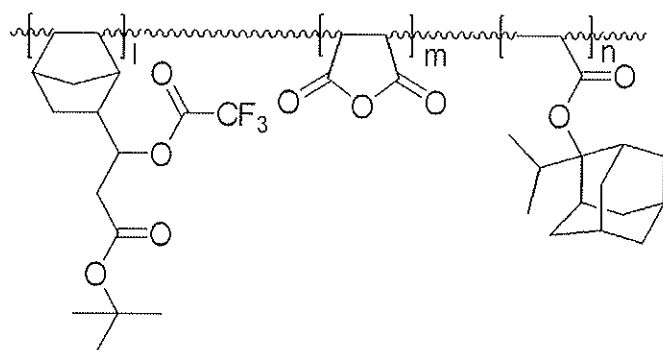


10

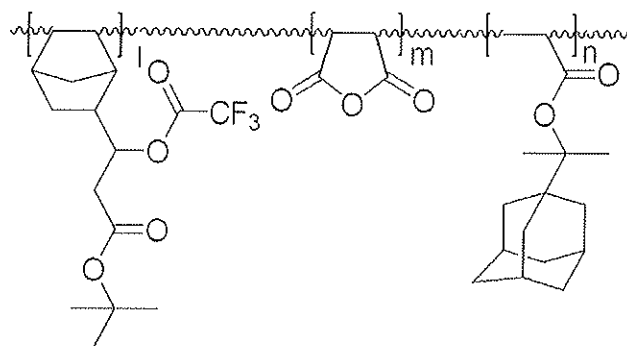
Formula 5



Formula 6

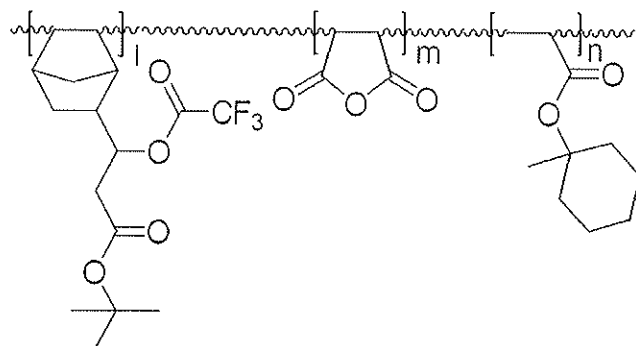


Formula 7

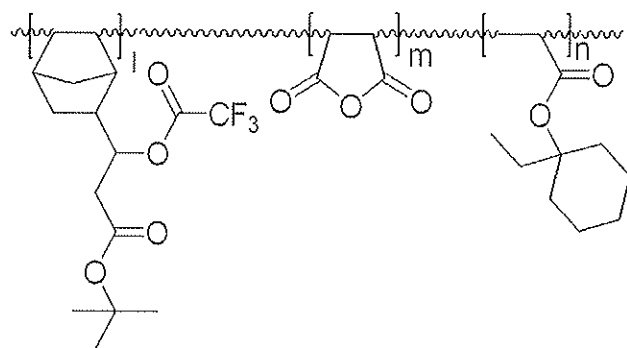


5

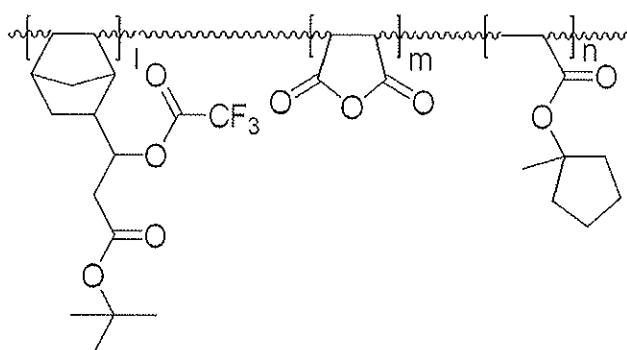
Formula 8



Formula 9

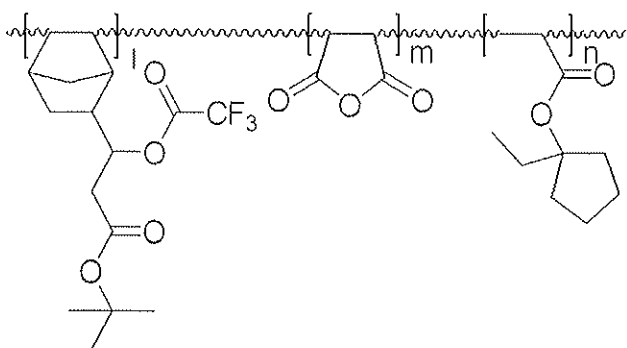


Formula 10



5

Formula 11



wherein l , m , and n are respectively numbers of the repeat units in a backbone, wherein $l+m+n=1$, $0 < l/(l+m+n) < 0.99$, $0 < m/(l+m+n) \leq 0.2$, and $0 < n/(l+m+n) < 0.99$.

10

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

5 9. 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 20,000 g/mol.

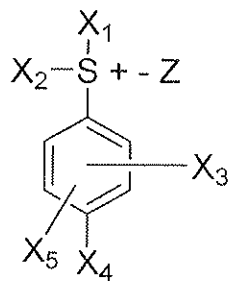
10 10. The resist additive of claim 1, wherein a weight average molecular weight/number average molecular weight ratio of the resist additive is in the range of 1 to 3.

15 11. A resist composition comprising a resist additive according to any one of claims 1 to 10, a resist base polymer, an acid generator, and a solvent.

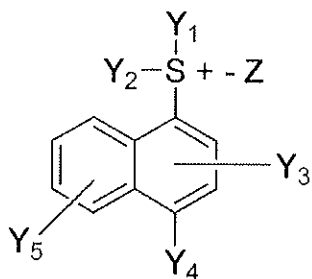
20 12. The resist composition of claim 11, wherein the amount of the resist additive is in the range of 0.05 to 5% by weight based on the total weight of the resist composition.

25 13. The resist composition of claim 11, wherein the acid generator comprises at least one compound selected from the group consisting of Formulae 14 and 15 below:

Formula 14



Formula 15

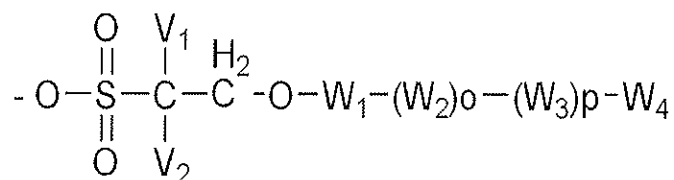


5 wherein X_1 , X_2 , Y_1 , and Y_2 are each independently selected from the group consisting of a hydrogen atom, a C1-C10 alkyl group, an allyl group, a perfluoroalkyl group, a benzyl group, a C6-C30 aryl group, and any combination thereof, wherein X_1 and X_2 are fused to form a C3-C30 saturated or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

15 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 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 16 below:

Formula 16



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,

W_3 is 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,

W_4 is 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,

o is an integer of 0 to 1, and

p is an integer of 0 to 2.

14. The resist composition of claim 11, 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.

15. The resist composition of claim 11, further
5 comprising an additive selected from the group consisting of an alkali soluble quencher, an acid diffusion quencher, a surfactant, and any mixture thereof.

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

forming a resist film by coating the resist composition according to claim 11 on a substrate;

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

15 developing the exposed pattern.

17. The method of claim 16, wherein the exposing is performed using a light source selected from the group consisting of a KrF excimer laser, an ArF excimer laser, an
20 extreme ultraviolet laser, an X-ray, and an electron beam.