METHOD OF FORMING PATTERN AND ACTINIC-RAY- OR RADIATION-SENSITIVE RESIN COMPOSITION

According to one embodiment, there is provided a method of forming a pattern, comprising (i) forming a film from an actinic-ray- or radiation-sensitive resin composition comprising a resin (P) containing at least one repeating unit (a) represented by at least one general formula (I) and (II) below and at least one repeating unit (b) represented by at least one general formulae (III), (IV) and (V) below and further comprising a compound (B) that generates an acid when exposed to actinic rays or radiation, (ii) exposing the film to light by means of a KrF excimer laser, and (iii) developing the exposed film with a developer containing an organic solvent, thereby forming a negative pattern.
Published:

with international search report (Art. 21(3))
DESCRIPTION

METHOD OF FORMING PATTERN AND ACTINIC-RAY-OR RADIATION-SENSITIVE RESIN COMPOSITION

Cross-Reference to Related Applications

This application is based upon and claims the benefit of priority from prior Japanese Patent Application No. 2011-143181, filed June 28, 2011, the entire contents of which are incorporated herein by reference.

Technical Field

The present invention relates to a method of forming a pattern that is suitable for use in lithography operations employed in a semiconductor production process for an IC or the like, the production of a circuit board for a liquid crystal, a thermal head or the like and other photofabrication, an actinic-ray- or radiation-sensitive resin composition for using in the method, and an actinic-ray- or radiation-sensitive film formed from the composition. Furthermore, the present invention relates to a process for manufacturing an electronic device using the method of forming a pattern and an electronic device manufactured using the process. The method of forming a pattern according to the present invention is particularly suitable for exposure using an KrF exposure apparatus.
Since the emergence of the resist for a KrF excimer laser (248 nm), it has been of common practice to employ an image forming method in which chemical amplification is utilized in order to compensate for any sensitivity decrease caused by light absorption. For example in a positive chemical amplification method as an image forming method, first, a photoacid generator contained in exposed areas is decomposed by light irradiation using an excimer laser, electron beams, extreme ultraviolet rays, etc. to thereby generate an acid. Then, in the stage of, for example, the bake after the exposure (Post-Exposure Bake: PEB), the generated acid is utilized as a catalyst of reaction so that the alkali-insoluble group contained in the photosensitive composition is converted to an alkali-soluble group. Thereafter, the exposed areas are removed using an alkali solution.

For use in the above method, various alkali developers have been proposed. For example, an aqueous alkali developer containing 2.38 mass% TMAH (aqueous solution of tetramethylammonium hydroxide) is generally used.

On the other hand, not only a positive patterning method which is currently mainstream but also a method using negative developer, namely, a developer containing an organic solvent is being exploited (see,
for example, patent references 1 to 3). These reflect
the situation in which in the production of
semiconductor elements and the like, while there is a
demand for the formation of a pattern with various
configurations, such as a line, a trench and a hole,
there exist patterns whose formation is difficult with
the use of current positive resists.

In recent years, the most advanced patterning
method under development comprises, in not only
positive patterning but also negative patterning,
exposure by means of an ArF excimer laser performed in
a liquid-immersion fashion so that a pattern of high
resolution can be formed. However, in semiconductor
manufacturing, there are demands for not only ultimate
miniaturization but also the effective utilization of
existing facilities and the promotion of cost
reduction. Accordingly, replacing part of a process
that was previously conducted by means of ArF exposure
with KrF exposure is now being studied. However, the
technology of ArF exposure has now superseded the
limits of KrF exposure. With respect to the above-
mentioned replacement of part of ArF exposure process
with KrF exposure, the current situation is that not
only is the above miniaturization to be coped with but
also there are a bunch of problems to be resolved, such
as the requirement for improving materials (resin,
etc.) for use and difficulty in solving technological
problems related to the difference in exposure mechanism, etc.

[Prior Art Reference]

[Patent reference]

2010-40849,

Disclosure of Invention

It is an object of the present invention to provide a method of forming a pattern, which method can be performed at low cost and excels in the capability of forming a pattern on uneven-surface substrates. It is another object of the present invention to provide an actinic-ray- or radiation-sensitive resin composition for use in the method.

Some aspects of the present invention are as follows.

[1] A method of forming a pattern, comprising:
(i) forming a film from an actinic-ray- or radiation-sensitive resin composition comprising a resin (P) containing at least one repeating unit (a) represented by at least one of general formula (I) and (II) below and at least one repeating unit (b) represented by at least one of general formulae (III), (IV) and (V) below and further comprising a compound
(B) that generates an acid when exposed to actinic rays or radiation;

(ii) exposing the film to light by means of a KrF excimer laser; and

(iii) developing the exposed film with a developer containing an organic solvent, thereby forming a negative pattern,

in which

each of $R_{11}$, $R_{21}$, $R_{31}$, $R_{41}$ and $R_{51}$ independently represents a hydrogen atom or a methyl group;

$R_{12}$ represents a hydrogen atom or a $-\text{COOCH}_3$ group;

$X$ represents a methylene group or an oxygen atom;

each of $R_{32}$, $R_{42}$ and $R_{52}$ independently represents an alkyl group having 1 to 4 carbon atoms;

$m$ is 0 or 1; and

$n$ is 1 or 2.

[2] The method according to [1], wherein the
repeating unit (a) comprises at least one repeating unit represented by the general formula (I) and the repeating unit (b) comprises at least one repeating unit represented by the general formula (IV).

[3] The method according to [1] or [2], wherein the organic solvent contained in the developer is at least one solvent selected from the group consisting of a ketone solvent, an ester solvent, an alcohol solvent, an amide solvent, an ether solvent and a hydrocarbon solvent.

[4] The method according to any one of [1] to [3], further comprising, to be performed after the development of the film with the developer, (iv) rinsing the film with a rinse liquid containing an organic solvent.

[5] The method according to any one of [1] to [4], wherein the negative pattern is formed on an uneven-surface substrate.


[7] An actinic-ray- or radiation-sensitive film formed from the actinic-ray- or radiation-sensitive resin composition according to [6].

[8] A process for manufacturing an electronic device comprising the method according to any one of [1] to [5].
An electronic device manufactured by the process according to [8].

The present invention has made it feasible to provide a method of forming a pattern, which method can be performed at low cost and excels in the capability of forming a pattern on uneven-surface substrates. The present invention has also made it feasible to provide an actinic-ray- or radiation-sensitive resin composition for use in the method.

Brief Description of Drawings

FIGS. 1A to 1G are views showing a method for fabricating an uneven-surface substrate.

Best Mode for Carrying Out the Invention

The present invention will be described below.

Note that, with respect to the expression of a group (or an atomic group) used in this specification, the expression without explicitly referring to whether the group is substituted or unsubstituted encompasses not only groups with no substituents but also groups having one or more substituents. For example, the expression "alkyl group" encompasses not only alkyl groups having no substituents (viz. unsubstituted alkyl groups) but also alkyl groups having one or more substituents (viz. substituted alkyl groups).

Method of forming pattern>

The method of forming a pattern according to the present invention comprises (1) forming into a film an
actinic-ray- or radiation-sensitive resin composition
comprising a resin (P) containing at least one
repeating unit (a) expressed by at least either general
formula (I) or (II) below and at least one repeating
unit (b) expressed by at least one of general formulae
(III), (IV) and (V) below and further comprising a
compound (b) that generates an acid when exposed to
actinic rays or radiation; (ii) exposing the film to
light by means of a KrF excimer laser; and (iii)
developing the exposed film with a developer containing
an organic solvent, thereby forming a negative pattern,

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} \\
\text{(III)} & \quad \text{(IV)} \\
\text{(V)} & \\
\end{align*}
\]

(in the formulae, each of \( R_{11}, R_{21}, R_{41}, R_{51} \) independently represents a hydrogen atom or a
methyl group; \( R_{12} \) represents a hydrogen atom or
a \(-\text{COOCH}_3\) group; \( X \) represents a methylene group or an
oxygen atom; each of \( R_{22}, R_{42}, R_{52} \) independently
represents an alkyl group having 1 to 4 carbon atoms; \( m \)
is 0 or 1; and n is 1 or 2).

Herein, the term "negative pattern" means a pattern obtained by negative development (development in which, due to a decrease of the solubility in a developer upon exposure to light, exposed areas remain as a pattern while unexposed areas are dissolved away).

The actinic-ray- or radiation-sensitive resin composition for use in the method of forming a pattern according to the present invention is one generally used in the patterning through ArF exposure. Therefore, in the method of forming a pattern according to the present invention, not only can a generally used inexpensive resin composition be employed but also the existing facilities for KrF exposure can be used, so that cost reduction can be attained. Moreover, the method of forming a pattern according to the present invention can produce a desirable pattern even in the patterning on uneven-surface substrates.

In the method of forming a pattern according to the present invention, the operation of forming a film of actinic-ray- or radiation-sensitive resin composition on a substrate, the operation of exposing the film to light and the operation of developing the exposed film can be performed through generally known procedures.

It is preferred for the developer for use in the method of forming a pattern according to the present
invention to be a developer (hereinafter also referred to as an organic developer) containing at least one organic solvent selected from the group consisting of a ketone solvent, an ester solvent, an alcohol solvent, an amide solvent, an ether solvent and a hydrocarbon solvent.

As the ketone solvent, there can be mentioned, for example, 1-octanone, 2-octanone, 1-nonanone, 2-nonanone, acetone, 2-heptanone (methyl amyl ketone), 4-heptanone, 1-hexanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, phenylacetone, methyl ethyl ketone, methyl isobutyl ketone, acetylacetone, acetonylacetone, ionone, diacetonyl alcohol, acetylcarbinol, acetophenone, methyl naphthyl ketone, isophorone, propylene carbonate or the like.

As the ester solvent, there can be mentioned, for example, methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, pentyl acetate, isopentyl acetate, amyl acetate, propylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethyl 3-ethoxypropionate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate or the like.

As the alcohol solvent, there can be mentioned,
for example, an alcohol, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol or n-decanol; a glycol solvent, such as ethylene glycol, diethylene glycol or triethylene glycol; or a glycol ether solvent, such as ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, diethylene glycol monomethyl ether, triethylene glycol monoethyl ether or methoxymethylbutanol.

As the ether solvent, there can be mentioned, for example, not only any of the above-mentioned glycol ether solvents but also dioxane, tetrahydrofuran or the like.

As the amide solvent, there can be mentioned, for example, N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, hexamethylphosphoronic triamide, 1,3-dimethyl-2-imidazolidinone or the like.

As the hydrocarbon solvent, there can be mentioned, for example, an aromatic hydrocarbon solvent, such as toluene or xylene, or an aliphatic hydrocarbon solvent, such as pentane, hexane, octane or decane.

Two or more of these solvents may be mixed together before use. Alternatively, each of the
solvents may be used in a mixture with water or a solvent other than those mentioned above. From the viewpoint of the fullest exertion of the effects of the present invention, it is preferred for the water content of the whole developer to be less than 10 mass%. More preferably, the developer substantially does not contain any water.

Namely, the content of organic solvent in the organic developer is preferably in the range of 90 to 100 mass%, more preferably 95 to 100 mass%, based on the total amount of the developer.

The vapor pressure of the organic developer at 20°C is preferably 5 kPa or below, more preferably 3 kPa or below and most preferably 2 kPa or below. When the vapor pressure of the organic developer is 5 kPa or below, the evaporation of the developer on a substrate or in a development cup can be suppressed so that the temperature uniformity within the plane of the wafer can be enhanced to thereby improve the dimensional uniformity within the plane of the wafer.

As particular examples of the organic developers exhibiting a vapor pressure of 5 kPa or below, there can be mentioned a ketone solvent, such as 1-octanone, 2-octanone, 1-nonanone, 2-nonanone, 2-heptanone (methyl amyl ketone), 4-heptanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, phenylacetone or methyl isobutyl ketone; an ester
solvent, such as butyl acetate, pentyl acetate, isopentyl acetate, amyl acetate, propylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethyl 3-ethoxypropionate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, butyl formate, propyl formate, ethyl lactate, butyl lactate or propyl lactate; an alcohol solvent, such as n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol or n-decanol; a glycol solvent, such as ethylene glycol, diethylene glycol or triethylene glycol; a glycol ether solvent, such as ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, diethylene glycol monomethyl ether, triethylene glycol monoethyl ether or methoxymethylbutanol; an ether solvent, such as tetrahydrofuran; an amide solvent, such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide or N,N-dimethylformamide; an aromatic hydrocarbon solvent, such as toluene or xylene, and an aliphatic hydrocarbon solvent, such as octane or decane.

As particular examples of the organic developers exhibiting a vapor pressure of 2 kPa or below representing an especially preferred range, there can
be mentioned a ketone solvent, such as 1-octanone, 2-octanone, 1-nonanone, 2-nonanone, 4-heptanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone or phenylacetone; an ester solvent, such as butyl acetate, amyl acetate, propylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, ethyl 3-ethoxypropionate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, ethyl lactate, butyl lactate or propyl lactate; an alcohol solvent, such as n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol or n-decanol; a glycol solvent, such as ethylene glycol, diethylene glycol or triethylene glycol; a glycol ether solvent, such as ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, diethylene glycol monomethyl ether, triethylene glycol monoethyl ether or methoxymethylbutanol; an amide solvent, such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide or N,N-dimethylformamide; an aromatic hydrocarbon solvent, such as xylene; and an aliphatic hydrocarbon solvent, such as octane or decane.

According to necessity, an appropriate amount of surfactant can be added to the organic developer.
The surfactant is not particularly limited. For example, use can be made of any of ionic and nonionic fluorinated and/or siliconized surfactants and the like. As such fluorinated and/or siliconized surfactants, there can be mentioned, for example, those described in JP-A's S62-36663, S61-226746, S61-226745, S62-170950, S63-34540, H7-230165, H8-62834, H9-54432 and H9-5988 and USPs 5405720, 5360692, 5529881, 5296330, 5436098, 5576143, 5294511 and 5824451.

Nonionic surfactants are preferred. Although nonionic surfactants are not particularly limited, using a nonionic fluorinated surfactant or siliconized surfactant is more preferred.

The amount of surfactant added is generally in the range of 0.001 to 5 mass%, preferably 0.005 to 2 mass% and further more preferably 0.01 to 0.5 mass% based on the whole amount of the developer.

As the development method, use can be made of, for example, a method in which the substrate is dipped in a tank filled with a developer for a given period of time (dip method), a method in which a developer is puddled on the surface of the substrate by its surface tension and allowed to stand still for a given period of time to thereby effect development (puddle method), a method in which a developer is sprayed onto the surface of the substrate (spray method), or a method in which a developer is continuously discharged onto the substrate.
being rotated at a given speed while scanning a developer discharge nozzle at a given speed (dynamic dispense method).

With respect to the above various development methods, when the operation of discharging a developer toward a resist film through a development nozzle of a development apparatus is included, the discharge pressure of discharged developer (flow rate per area of discharged developer) is preferably 2 ml/sec/mm^2 or below, more preferably 1.5 ml/sec/mm^2 or below and further more preferably 1 ml/sec/mm^2 or below. There is no particular lower limit of the flow rate. However, from the viewpoint of through-put, it is preferred for the flow rate to be 0.2 ml/sec/mm^2 or higher.

Pattern defects attributed to any resist residue after development can be markedly reduced by regulating the discharge pressure of discharged developer so as to fall within the above range.

The details of the mechanism thereof have not been elucidated. However, it is presumed that regulating the discharge pressure so as to fall within the above range would decrease the pressure of the developer on the resist film, thereby inhibiting any inadvertent shaving or crumbling of the resist film/resist pattern.

The discharge pressure of developer (ml/sec/mm^2) refers to a value exhibited at the outlet of the
development nozzle of the development apparatus.

For the regulation of the discharge pressure of developer, there can be employed, for example, a method in which the discharge pressure is regulated by means of a pump or the like, or a method in which the discharge pressure is changed through pressure regulation by supply from a pressure tank.

The operation of developing with a developer containing an organic solvent may be followed by the operation of discontinuing the development by replacement with another solvent.

The method of forming a pattern according to the present invention may further include (d) the operation of rinsing the developed film with a rinse liquid containing an organic solvent to be conducted after the operation of developing with a developer containing an organic solvent.

The rinse liquid for use in the rinse operation after the development operation is not particularly limited as long as it does not dissolve the resist pattern, and solutions containing common organic solvents can be used as the same. It is preferred for the rinse liquid to be one containing at least one organic solvent selected from the group consisting of a hydrocarbon solvent, a ketone solvent, an ester solvent, an alcohol solvent, an amide solvent and an ether solvent.
Particular examples of the hydrocarbon solvent, ketone solvent, ester solvent, alcohol solvent, amide solvent and ether solvent are the same as set forth above in connection with the developer containing an organic solvent.

The operation of developing with the developer containing an organic solvent is preferably followed by the operation of rinsing with a rinse liquid containing at least one organic solvent selected from the group consisting of a ketone solvent, an ester solvent, an alcohol solvent and an amide solvent; more preferably followed by the operation of rinsing with a rinse liquid containing an alcohol solvent or an ester solvent; further more preferably followed by the operation of rinsing with a rinse liquid containing a monohydric alcohol; and most preferably followed by the operation of rinsing with a rinse liquid containing a monohydric alcohol having 5 or more carbon atoms.

As the monohydric alcohol for use in the rinse operation, there can be mentioned a linear, branched or cyclic monohydric alcohol. Particular examples thereof include 1-butanol, 2-butanol, 3-methyl-1-butanol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 1-hexanol, 4-methyl-2-pentanol, 1-heptanol, 1-octanol, 2-hexanol, cyclopentanol, 2-heptanol, 2-octanol, 3-hexanol, 3-heptanol, 3-octanol and 4-octanol. Particular examples of the most preferred monohydric alcohols each having 5
or more carbon atoms include 1-hexanol, 2-hexanol, 4-
methyl-2-pentanol, 1-pentanol and 3-methyl-1-butanol.

Two or more of these components may be mixed together before use. Also, they may be mixed with other organic solvents before use.

The water content of the rinse liquid is preferably 10 mass% or below, more preferably 5 mass% or below and most preferably 3 mass% or below. A favorable development performance can be attained by controlling the water content of the rinse liquid at 10 mass% or below.

With respect to the rinse liquid for use after the operation of developing with a developer containing an organic solvent, the vapor pressure thereof at 20°C is preferably in the range of 0.05 to 5 kPa, more preferably 0.1 to 5 kPa and most preferably 0.12 to 3 kPa. When the vapor pressure of the rinse liquid is in the range of 0.05 to 5 kPa, not only can the temperature uniformity within the plane of the wafer be enhanced but also the swell attributed to the penetration of the rinse liquid can be suppressed to thereby improve the dimensional uniformity within the plane of the wafer.

An appropriate amount of surfactant may be added to the rinse liquid before use.

In the rinse operation, the wafer having undergone the development with a developer containing an organic
solvent is rinsed using the above rinse liquid containing an organic solvent. The method of rinse treatment is not particularly limited. For example, use can be made of any of a method in which the rinse liquid is continuously applied onto the substrate being rotated at a given speed (spin application method), a method in which the substrate is dipped in a tank filled with the rinse liquid for a given period of time (dip method) and a method in which the rinse liquid is sprayed onto the surface of the substrate (spray method). Preferably, the rinse treatment is carried out according to the spin application method, and thereafter the substrate is rotated at a rotating speed of 2000 to 4000 rpm to thereby remove the rinse liquid from the top of the substrate. Also, preferably, a baking operation (post-bake) is carried out subsequent to the rinse operation. Any inter-pattern and intra-pattern remaining developer and rinse liquid are removed by carrying out the bake. The postbake operation subsequent to the rinse operation is generally performed at 40 to 160°C, preferably 70 to 95°C, for a period of 10 seconds to 3 minutes, preferably 30 to 90 seconds.

In the method of forming a pattern according to the present invention, a pre-bake (PB) operation is preferably carried out after the operation of film formation but prior to the exposure operation.
Also preferably, a post-exposure bake (PEB) is carried out after the exposure operation but prior to the development operation.

In both PB and PEB operations, the bake is preferably carried out at 70 to 120°C, more preferably 80 to 110°C.

The baking time is preferably in the range of 30 to 300 seconds, more preferably 30 to 180 seconds and further more preferably 30 to 90 seconds.

The baking can be carried out using means provided in common exposure/development equipment. The baking may also be carried out using a hot plate or the like.

The baking accelerates the reaction in exposed areas, thereby enhancing the sensitivity and pattern profile.

The pattern forming method of the present invention can include a plurality of baking operations.

The pattern forming method of the present invention may further include the operation of developing with an alkali developer.

When the method of forming a pattern according to the present invention further includes the operation of developing with an alkali developer, as the alkali developer, use can be made of, for example, any of alkaline aqueous solutions of an inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate or
aqueous ammonia, a primary amine such as ethylamine or n-propylamine, a secondary amine such as diethylamine or di-n-butylamine, a tertiary amine such as triethylamine or methyldiethylamine, an alcoholamine such as dimethylethanolamine or triethanolamine, a quaternary ammonium salt such as tetramethylammonium hydroxide or tetraethylammonium hydroxide, a cycloamine such as pyrrole or piperidine, and the like.

Appropriate amounts of an alcohol and a surfactant may be added to the above alkaline aqueous solutions before the use thereof.

The alkali concentration of the alkali developer is generally in the range of 0.1 to 20 mass%.

The pH value of the alkali developer is generally in the range of 10.0 to 15.0.

A 2.38 mass% aqueous tetramethylammonium hydroxide solution is particularly preferred.

Pure water is used as the rinse liquid for use in the rinse treatment after the alkali development.

Before the use thereof, an appropriate amount of surfactant may be added thereto.

Further, the development operation or rinse operation may be followed by the operation of removing any portion of developer or rinse liquid adhering onto the pattern by use of a supercritical fluid.

The method of forming a pattern according to the present invention can include a plurality of exposure...
It is preferred for the wavelength of the light source for use in the exposure apparatus in the present invention to be that of a KrF excimer laser (248 nm).

The substrate for forming a film in the present invention is not particularly limited. Use can be made of substrates commonly employed in a semiconductor production process for an IC or the like, a circuit board production process for a liquid crystal, a thermal head or the like and other photoapplication lithography processes, for example, inorganic substrates of silicon, SiN, SiO2 and the like, and coated inorganic substrates, such as SOG. Further, according to necessity, an organic antireflection film may be provided between the film and the substrate.

For example, an antireflection film may be provided as an underlayer of the resist. As the antireflection film, use can be made of both an inorganic film of titanium, titanium oxide, titanium nitride, chromium oxide, carbon, amorphous silicon or the like and an organic film composed of a light absorber and a polymer material. The former film in the stage of film formation requires equipment, such as a vacuum vapor deposition apparatus, a CVD apparatus or a sputtering apparatus. As the organic antireflection film, there can be mentioned, for example, one composed of a condensate of diphenylamine derivative and
formaldehyde modified melamine resin, an alkali-soluble resin and a light absorber as described in Jpn. Pat. Appln. KOKOKU Publication No. 7-69611; one consisting of a product of reaction between a maleic anhydride copolymer and a diamine light absorber as described in USP 5294680; one containing a resin binder and a methylolmelamine thermal crosslinking agent as described in JP-A-6-118631; an acrylic resin antireflection film simultaneously having a carboxylic acid group, an epoxy group and a light absorbing group in each molecule thereof as described in JP-A-6-118656; one composed of a methylolmelamine and a benzophenone light absorber as described in JP-A-8-87115; one obtained by adding a low-molecular light absorber to a polyvinyl alcohol resin as described in JP-A-8-179509; or the like.

Also, as the organic antireflection film, use can be made of commercially available organic antireflection films, such as DUV30 Series and DUV40 Series produced by Brewer Science Inc. and AR-2, AR-3 and AR-5 produced by Shipley Co., Ltd.

Further, according to necessity, an antireflection film can be provided as an upper layer of the resist.

As the antireflection film, there can be mentioned, for example, AQUATAR-I, AQUATAR-III, AQUATAR-VII, etc. manufactured by AZ Electronic Materials Co., Ltd.
The present invention also relates to a process for manufacturing an electronic device in which the above pattern forming method of the present invention is included and to an electronic device manufactured by the process.

The electronic device of the present invention can be appropriately mounted in electrical and electronic equipment (household electronic appliance, OA/media-related equipment, optical apparatus and telecommunication equipment).

<Actinic-ray- or radiation-sensitive resin composition>

The actinic-ray- or radiation-sensitive resin composition that can be used in the method of forming a pattern according to the present invention will be described below.

The actinic-ray- or radiation-sensitive resin composition according to the present invention is used in negative development (development in which, due to a decrease of the solubility in a developer upon exposure to light, exposed areas remain as a pattern while unexposed areas are dissolved away). Namely, the actinic-ray- or radiation-sensitive resin composition according to the present invention can be an actinic-ray- or radiation-sensitive resin composition for organic solvent development that is used in development using a developer containing an organic solvent.
Herein, the expression "for organic solvent development" means usage involving the application to at least the operation of developing with a developer containing an organic solvent.

The actinic-ray- or radiation-sensitive resin composition according to the present invention is typically a resist composition. From the viewpoint that especially high effects can be attained, it is preferred for the same to be a negative resist composition (namely, resist composition for organic solvent development). Moreover, the composition according to the present invention is typically a chemically amplified resist composition, especially a resist composition for KrF exposure.

The actinic-ray- or radiation-sensitive resin composition according to the present invention comprises a resin (P) that decreases its solubility in a developer containing an organic solvent when acted on by an acid, and a compound (B) that generates an acid when exposed to actinic rays or radiation. Further, this resist composition may contain at least one member selected from among a solvent, a basic compound, a surfactant and other additives. These components of the composition will be described in sequence below.

[1] Resin (P)

The resin (P) is a resin that decreases its solubility in a developer containing an organic solvent.
when acted on by an acid and contains at least one repeating unit (a) represented by at least either general formula (I) or (II) below and at least one repeating unit (b) represented by at least one of general formulae (III), (IV) and (V) below. The repeating unit (b) is a repeating unit containing a group (hereinafter also referred to as an acid-decomposable group) that is decomposed to thereby produce a polar group when acted on by an acid. The acid-decomposable group may be positioned in the principal chain or a side chain of the resin (P) or in both the principal chain and a side chain. The repeating unit (a) is a repeating unit with a lactone structure. When a repeating unit with a lactone group is contained in the resin (P), the dissolution contrast in a developer containing an organic solvent can be enhanced. Further, by virtue of the employment of a specified lactone structure, a favorable pattern formation can be realized on uneven-surface substrates.
In the above general formulae, each of $R_{31, 41, 41'}$ and $R_{51}$ independently represents a hydrogen atom or a methyl group.

$R_{12}$ represents a hydrogen atom or a $-\text{COOCH}_3$ group.

$X$ represents a methylene group or an oxygen atom.

Each of $R_{32, 42, 52}$ independently represents an alkyl group having 1 to 4 carbon atoms.

As the alkyl group having 1 to 4 carbon atoms represented by each of $R_{32, 42, 52}$ there can be mentioned a linear or branched alkyl group having 1 to 4 carbon atoms. In particular, there can be mentioned a methyl group, an ethyl group, an $n$-propyl group, an isopropyl group, an $n$-butyl group, an isobutyl group or a tert-butyl group.

$R_{32}$ is preferably a methyl group, an ethyl group, an $n$-propyl group or an isopropyl group, more preferably a methyl group, an ethyl group or an isopropyl group.

$R_{42}$ is preferably a methyl group, an ethyl group, an $n$-propyl group or an isopropyl group, more preferably a methyl group, an ethyl group or an isopropyl group. A methyl group and an ethyl group are...
most preferred.

R52 is preferably a methyl group, an ethyl group, an n-propyl group or an isopropyl group, more preferably a methyl group, an ethyl group or an isopropyl group. A methyl group and an ethyl group are most preferred.

In the formulae, m is 0 or 1, and n is 1 or 2.

The content of repeating unit (a) (when a plurality of different repeating units (a) are contained, the sum thereof) in the resin (P) according to the present invention is not particularly limited. However, from the viewpoint of the secure attainment of the effects of the present invention, the content based on all the repeating units of the resin (P) is preferably 20 mol% or more, more preferably 25 mol% or more, and most preferably 30 mol% or more. There is no particular upper limit of the content. However, from the viewpoint of the formation of a desirable pattern, the content is preferably 90 mol% or below, more preferably 85 mol% or below.

The content of repeating unit (b) (when a plurality of different repeating units (b) are contained, the sum thereof) is not particularly limited. However, from the viewpoint of the secure attainment of the effects of the present invention, the content based on all the repeating units of the resin (P) is preferably 30 moll or more, more preferably
35 mol% or more, and most preferably 40 mol% or more. There is no particular upper limit of the content. However, from the viewpoint of the formation of a desirable pattern, the content is preferably 90 mol% or below, more preferably 85 mol% or below.

Further, from the viewpoint of the secure attainment of the effects of the present invention, the sum of the content of repeating unit (a) (when a plurality of different repeating units (a) are contained, the sum thereof) and the content of repeating unit (b) (when a plurality of different repeating units (b) are contained, the sum thereof) based on all the repeating units of the resin (P) is preferably 50 mol% or more, more preferably 65 mol% or more, and most preferably 70 mol% or more.

Specific examples of the repeating units (a) of general formulae (I) and (II) above and specific examples of the repeating units (b) of general formulae (III) to (V) above are shown below, which however in no way limit the scope of the present invention.
specific examples of general formulae (I)

specific examples of general formulae (II)

specific examples of general formulae (III)
It is preferable that the repeating unit (a) includes at least one repeating unit represented by the general formula (I) and the repeating unit (b) includes at least one repeating unit represented by the general formula (IV).

The resin (P) can contain, in addition to the foregoing repeating units (a) and (b), various repeating structural units for the purpose of regulating the dry etching resistance, standard
developer adaptability, substrate adhesion, resist profile and generally required properties of the resist such as resolving power, heat resistance and sensitivity. The resin (P) may be a blend of two or more different resins (P).

Repeating units other than the repeating units (a) and (b) that can be contained in the resin (P) will be described below.

[Repeating unit containing acid-decomposable group]

The resin (P) may further contain a repeating unit containing a group that is decomposed when acted on by an acid to thereby produce a polar group (namely, an acid-decomposable group), other than the repeating unit (b).

When the resin (P) according to the present invention contains a repeating unit containing an acid-decomposable group other than the repeating unit (b), the content of the sum of the same and the repeating unit (b) based on all the repeating units of the resin (P) is preferably 30 mol% or more, more preferably 35 mol% or more, and most preferably 40 mol% or more. There is no particular upper limit of the content. However, from the viewpoint of the formation of a desirable pattern, the content is preferably 90 mol% or below, more preferably 85 mol% or below.
The resin (P) may further contain a repeating unit with a lactone structure other than the repeating unit (a). When the resin (P) according to the present invention contains a repeating unit with a lactone structure other than the repeating unit (a), the content of the sum of the same and the repeating unit (a) based on all the repeating units of the resin (P) is preferably 20 mol% or more, more preferably 25 mol% or more, and most preferably 30 mol% or more. There is no particular upper limit of the content. However, from the viewpoint of the formation of a desirable pattern, the content is preferably 90 mol% or below, more preferably 85 mol% or below.

[Other repeating unit]

The resin (P) may further contain a repeating unit containing a polar group (for example, a hydroxyl group, a cyano group, a carboxyl group or the like), a repeating unit with an alicyclic hydrocarbon structure having no polar group (for example, a cyclohexyl group, a norbornyl group, an adamantyl group, a tricyclodecanyl group or the like) that exhibits no acid decomposability and a repeating unit obtained by polymerization of a compound having an unsaturated bond capable of addition polymerization (for example, an acrylic ester, a methacrylic ester, an acrylamide, a
methacrylamide, an allyl compound, a vinyl ether, a vinyl ester or the like). Containing these other repeating units enhances the adherence to substrates and developer affinity.

When the resin (P) further contains these other repeating units, the content thereof based on all the repeating units of the resin (P) is preferably in the range of 1 to 30 mol%, more preferably 3 to 20 mol% and further more preferably 5 to 15 mol%.

The resin (P) according to the present invention can be synthesized in accordance with routine methods (for example, radical polymerization). As general synthesizing methods, there can be mentioned, for example, a batch polymerization method in which a monomer species and an initiator are dissolved in a solvent and heated to thereby carry out polymerization, a dropping polymerization method in which a solution of monomer species and initiator is dropped into a heated solvent over a period of 1 to 10 hours, and the like.

The dropping polymerization method is preferred. As a reaction solvent, there can be mentioned, for example, an ether such as tetrahydrofuran, 1,4-dioxane or diisopropyl ether, a ketone such as methyl ethyl ketone or methyl isobutyl ketone, an ester solvent such as ethyl acetate, an amide solvent such as dimethylformamide or dimethylacetamide, or the solvent capable of dissolving the composition of the present
invention, such as propylene glycol monomethyl ether acetate, propylene glycol monomethyl ether or cyclohexanone, to be described hereinafter. Preferably, the polymerization is carried out with the use of the same solvent as that used in the photosensitive composition according to the present invention. This would inhibit any particle generation during storage.

The polymerization reaction is preferably carried out in an atmosphere comprised of an inert gas, such as nitrogen or argon. The polymerization is initiated by use of a commercially available radical initiator (azo initiator, peroxide, etc.) as a polymerization initiator. Among the radical initiators, an azo initiator is preferred, and azo initiators having an ester group, a cyano group and a carboxyl group are especially preferred. As specific preferred initiators, there can be mentioned azobisisobutyronitrile, azobisdimethylvaleronitrile, dimethyl 2,2'-azobis (2-methylpropionate) and the like. If desirable, the initiator may be supplemented, or may be added in fractional amounts. After the completion of the reaction, the reaction liquid is poured into a solvent, and the intended polymer is recovered by a method of powder or solid recovery or the like. The reaction concentration is in the range of 5 to 50 mass%, preferably 10 to 30 mass%. The reaction
temperature is generally in the range of 10 to 150°C, preferably 30 to 120°C and more preferably 60 to 100°C.

The weight average molecular weight of the resin (P), in terms of polystyrene-equivalent value measured by GPC, is preferably in the range of 1000 to 200,000. It is more preferably in the range of 2000 to 70,000, further more preferably 3000 to 50,000 and most preferably 5000 to 30,000. By regulating the weight average molecular weight so as to fall within the range of 1000 to 200,000, not only can any deterioration of heat resistance and dry etching resistance be prevented but also any deterioration of developability and any increase of viscosity leading to poor film forming property can be prevented.

The polydispersity index (molecular weight distribution) of the resin is generally in the range of 1 to 3, preferably 1 to 2.6, more preferably 1 to 2 and most preferably 1.4 to 2.0. The narrower the molecular weight distribution, the easier the pattern formation on uneven-surface substrates.

In the present invention, the amount of resin (P) contained in the whole composition is preferably in the range of 30 to 99 mass%, more preferably 60 to 95 mass%, based on the total solids of the composition.

One type of resin according to the present invention may be used alone, or two or more types thereof may be used in combination. Resins other than
the above resins (P) may be used in combination therewith in an amount not detrimental to the effects of the present invention.

Particular examples of the resins (P) are shown below.
[a compound (B) that generates an acid when exposed to actinic rays or radiation]

The actinic-ray- or radiation-sensitive resin composition according to the present invention may contain a compound (B) that generates an acid when exposed to actinic rays or radiation (hereinafter referred to as an acid generator (B)). As the acid generator (B), use can be made of a member appropriately selected from among a photoinitiator for photocationic polymerization, a photoinitiator for photoradical polymerization, a photo-achromatic agent and photo-discoloring agent for dyes, any of publicly
known compounds that generate an acid when exposed to actinic rays or radiation employed in microresists, etc., and mixtures thereof.

As the acid generator (B), a diazonium salt, a phosphonium salt, a sulfonium salt, an iodonium salt, an imide sulfonate, an oxime sulfonate, diazosulfone, disulfone and o-nitrobenzyl sulfonate can be exemplified. Preferably, the acid generator (B) contains a sulfonium salt or an iodonium salt.

Further, use can be made of compounds obtained by introducing any of the above groups or compounds that generate an acid when exposed to actinic rays or radiation in a polymer principal chain or side chain, for example, compounds described in USP 3,849,137, DE 3914407, JP-A's-63-26653, 55-164824, 62-69263, 63-146038, 63-163452, 62-153853, 63-146029, etc.

Furthermore, use can be made of compounds that generate an acid when exposed to light described in USP 3,779,778, EP 126,712, etc.

As preferred compounds among the compound that generates an acid when exposed to actinic rays or radiation as acid generators (B), those represented by the following general formulae (ZI), (ZII) and (ZIII) can be exemplified.
In the above general formula (ZI), each of R201', R202 and R203 independently represents an organic group.

\[ Z^- \text{ represents a nonnucleophilic anion.} \]

As the nonnucleophilic anion represented by $Z^-$, a sulfonate anion, a bis (alkylsulfonyl)amido anion, a tris (alkylsulfonyl) methyl anion, BF4^−, PF6^−, and SbF6^− can be exemplified. $Z^-$ preferably is an organic anion containing one or more carbon atoms. As the preferred organic anions, any of those represented by the following AN1 to AN3 can be exemplified.

<table>
<thead>
<tr>
<th>AN1</th>
<th>AN2</th>
<th>AN3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Rc_1SO_2$</td>
<td>$Rc_2SO_2^-$</td>
<td>$Rc_3SO_2^-$</td>
</tr>
<tr>
<td>$Rc_1S_03^e$</td>
<td>$N^e$</td>
<td>$Rc_2S_02^e$</td>
</tr>
</tbody>
</table>

In the formulae AN1 to AN3, $Rc_1$ to $Rc_3$ each independently represents an organic group. As the organic group, those having 1 to 30 carbon atoms can be exemplified. Preferably, a substituted or unsubstituted alkyl group, a monocyclic or polycyclic cycloalkyl group, a hetero atom containing cyclic group, aryl group, or a group in which these groups are connected through a single bond or a connecting group. As the connecting group, for example, -O-, -CO2-, -S-, -SO3- and -SO2N(Rd_1)- can be exemplified. Furthermore, these groups may form a ring together with a binding alkyl or aryl group.

Here, Rd_1 represents a hydrogen atom or an alkyl
group, and may form a ring together with a binding alkyl or aryl group.

An organic group represented by \( R_c^t \) to \( RC_3 \) may be an alkyl group whose 1-position is substituted with a fluorine atom or a fluoroalkyl group; or a phenyl group substituted with a fluorine atom or a fluoroalkyl group. Presence of a fluorine atom or a fluoroalkyl group can make an acidity of the acid generated by irradiating light become higher. This can enhance the sensitivity of the composition. When \( R_c^t \) to \( RC_3 \) contains five or more carbon atoms, at least one of the carbon atoms is preferably substituted with hydrogen atom(s) and the number of hydrogen atoms is preferably larger than the number of fluorine atoms. The toxicity to a living body can be reduced when any perfluoroalkyl groups having five or more carbon atoms are not contained in \( R_c^t \) to \( RC_3 \).

The number of carbon atoms in the organic group represented by \( R_{201} \) to \( R_{202} \) and \( R_{203} \) is generally in the range of 1 to 30, preferably 1 to 20.

Two of \( R_{201} \) to \( R_{203} \) may be bonded to each other thereby to form a ring. An oxygen atom, a sulfur atom, an ether bond, an amido bond, and a carbonyl group can be contained in the ring. As the group formed by bonding of two of \( R_{201} \) to \( R_{203} \) for example, an alkylene group such as a butylene group or a pentylene group can be exemplified.
As the specific examples of organic groups as 
R201' ^202' and ^203' corresponding groups in the 
compounds (ZI-1), (ZI-2), or (ZI-3) described below can 
be exemplified.

Appropriate use may be made of compounds with two 
or more of the structures represented by the general 
formula (ZI). For example, use may be made of 
compounds having a structure wherein at least one of 
R201 to R203 °f a compound represented by the general 
formula (ZI) is bonded to at least one of R20I to R203 
of another compound represented by the general 
formula (ZI).

As preferred (ZI) components, the following 
compounds (ZI-1) and (ZI-2) can be exemplified.

The compounds (ZI-1) are arylsulfonium compounds 
of the general formula (ZI) wherein at least one of 
R201 to R203 is an aryl group, namely, compounds 
containing an arylsulfonium as a cation.

In the arylsulfonium compounds, all of the R20I to 
R203 may be aryl groups. It is also appropriate that 
the R20I to R203 are partially an aryl group and the 
remainder is an alkyl group or a cycloalkyl group.

As the arylsulfonium compound, there can be 
mentioned, for example, a triarylsulfonium compound, a 
diarylalkylsulfonium compound, and an 
aryldialkylsulfonium compound.

An aryl group in the arylsulfonium compound is
preferably an aryl group such as a phenyl group, a naphthyl group, and a fluorene group, or a heteroaryl group such as an indole group and a pyrrole group. Of these, a phenyl group or an indole group is particularly preferred. When the arylsulfonium compound contains two or more aryl groups, these may either be identical to or different from each other.

The alkyl group or cycloalkyl group contained in the arylsulfonium compound according to necessity is preferably a linear or branched alkyl group having 1 to 15 carbon atoms or a cycloalkyl group having 3 to 15 carbon atoms. As such, there can be mentioned, for example, a methyl group, an ethyl group, a propyl group, an n-butyl group, a sec-butyl group, a t-butyl group, a cyclopropyl group, a cyclobutyl group, a cyclohexyl group or the like.

The aryl group, alkyl group or cycloalkyl group represented by R201 to R203 may have one or more substituents. As the substituent, an alkyl group (for example, 1 to 15 carbon atoms), a cycloalkyl group (for example, 3 to 15 carbon atoms), an aryl group (for example, 6 to 14 carbon atoms), an alkoxy group (for example, 1 to 15 carbon atoms), a halogen atom, a hydroxy group, and a phenylthio group can be exemplified.

Preferred substituents are a linear or branched alkyl group having 1 to 12 carbon atoms, a cycloalkyl
group having 3 to 12 carbon atoms and a linear, branched or cyclic alkoxy group having 1 to 12 carbon atoms. More preferred substituents are an alkyl group having 1 to 4 carbon atoms and an alkoxy group having 1 to 4 carbon atoms. The substituents may be contained in any one of the three R201 to R203 or alternatively may be contained in all three of R201 to R203. When R201 to R203 represent an aryl group, the substituent preferably lies at the p-position of the aryl group.

Now, the compounds (ZI-2) will be described.

The compounds (ZI-2) are compounds of formula (ZI) wherein each of R201 to R203 independently represents an organic group having no aromatic ring. The aromatic rings include an aromatic ring having a heteroatom.

The organic group having no aromatic ring represented by R201 to R203 generally has 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms.

Preferably, each of R201 to R203 independently represents an alkyl group, a cycloalkyl group, a 2-oxoalkyl group, a 2-oxocycloalkyl group, an alkoxy carbonylmethyl group, an allyl group or a vinyl group. More preferred groups are a linear or branched 2-oxoalkyl group, a 2-oxocycloalkyl group and an alkoxy carbonylmethyl group. Especially preferred is a linear or branched 2-oxoalkyl group.

As preferred alkyl groups and cycloalkyl groups represented by R201 to R203' there can be mentioned a
linear or branched alkyl group having 1 to 10 carbon atoms (for example, a methyl group, an ethyl group, a propyl group, a butyl group or a pentyl group) and a cycloalkyl group having 3 to 10 carbon atoms (a cyclopentyl group, a cyclohexyl group or a norbornyl group).

The 2-oxoalkyl group as R201 to R203 may be linear or branched. A group having >C=0 at the 2-position of the alkyl group is preferred.

The 2-oxocycloalkyl group as R201 to R203 is preferably a group having >C=0 at the 2-position of the cycloalkyl group.

As preferred alkoxy moieties in the alkoxy carbonylmethyl group, there can be mentioned alkoxy groups having 1 to 5 carbon atoms (a methoxy group, an ethoxy group, a propoxy group, a butoxy group and a pentoxy group).

The R201 to R203 may be further substituted with a halogen atom, an alkoxy group (for example, 1 to 5 carbon atoms), a hydroxyl group, a cyano group and/or a nitro group.

Two of R201 to R203 may be bonded to each other to thereby form a ring structure, and the ring within the same may contain an oxygen atom, a sulfur atom, an ester bond, an amido bond or a carbonyl group. As the group formed by the ring formation, an alkylene group such as a butylene group and a pentylene group can be
Explanations on general formula (ZII) and (ZIII) will follow.

In the general formulae (ZII) and (ZIII), each of R204 to R207 independently represents an aryl group, an alkyl group or a cycloalkyl group. These groups can contain one or more substituents.

As preferred aryl group represented by R204 to R207', those explained for R201 to R203 in the compounds (ZI-1) can be exemplified.

As preferred alkyl group and cycloalkyl group, those explained for R201 to R203 in the compounds (ZI-2) can be exemplified.

Z in the general formulae (ZII) and (ZIII) is the same as in the general formula (ZI).

As other examples of the compound that generates an acid when exposed to actinic rays or radiation as the photoacid generator (B), compounds represented by the following general formula (ZIV), (ZV) or (ZVI) can be exemplified.

\[
\begin{align*}
\text{ZIV} & : \quad \text{Ar}_3\text{SO}_2\text{SO}_2\text{Ar} \\
\text{ZV} & : \quad \text{R}_{206}\text{SO}_2\text{O} - \text{N} \quad \text{A} \\
\text{ZVI} & : \quad \text{N} - \text{SO}_2\text{R}_{208}
\end{align*}
\]

In the general formulae (ZIV) to (ZVI), each of \( \text{Ar}_3 \) and \( \text{Ar}_4 \) independently represents a substituted or unsubstituted aryl group.
Each of R208 independently represents an alkyl group, a cycloalkyl group or an aryl group. These groups may either be substituted or unsubstituted.

It is preferable for these groups to be substituted with one or more fluorine atoms. This leads to higher acidity of an acid generated by the photoacid generator.

Each of R209 and R210 independently represents an alkyl group, a cycoalkyl group, an aryl group, an alkylthio group or an electron-withdrawing group. These groups may either be substituted or unsubstituted. R209 and R210 may be bonded to each other to thereby form a ring structure, and the ring within the same may contain an oxygen atom, a sulfur atom, an alkylene group, an alkenylene group or an arylene group.

As preferred R209' a substituted or unsubstituted aryl group can be exemplified. As preferred R210, electron-withdrawing groups can be exemplified. As such, a cyano group or a fluoroalkyl group is more preferable.

A represents an alkylene group, a cycloalkylene group, an alkenylene group, or an arylene group. These groups may contain one or more substituents.

As specific examples of the aryl group represented by Ar3, Ar4, R208, R209 and R210 for example, the same aryl group as explained with respect to R201, R202 and
R203 can be exemplified.

As specific examples of the alkyl group and the cycloalkyl group represented by R208' ²09 and ²10' for example, the same alkyl group and the cycloalkyl group as explained with respect to R201' ¾02 and ²03 in the general formula (ZI-2) can be exemplified.

As specific examples of the alkyl moiety of the alkylthio group represented by R209 and R210' for example, the same alkyl group as explained with respect to R201' ²02 and ¾03 in the general formula (ZI-2) can be exemplified.

As the alkylene group represented by A, for example, the one having 1 to 12 carbon atoms such as a methylene group, an ethylene group, a propylene group, an isopropylene group, a butylene group, an isobutylene group, or the like can be exemplified. As the cycloalkylene group represented by A, for example, a monocyclic or polycyclic cycloalkylene group having 3 to 12 carbon atoms such as a cyclohexylene group, a norbornylene group, adamantylene group, or the like can be exemplified. As the alkenylene group represented by A, for example, the one having 2 to 12 carbon atoms such as an ethenylene group, a propenylene group, a butenylene group, or the like can be exemplified. As the arylene group represented by A, for example, the one having 6 to 10 carbon atoms such as a phenylene group, a tolylene group, a naphthylene group, or the
like can be exemplified. Also, compounds each with a plurality of structures expressed by general formula (ZVI) can preferably be used in the present invention. For example, a compound with a structure in which either R209 or R210 of a compound of general formula (ZVI) is bonded to either R209 or R210 of another compound of general formula (ZVI) can preferably be used.

Among the compounds that are decomposed when exposed to actinic rays or radiation to thereby generate acids as acid generators (B), the compounds of general formulae (ZIII) to (ZVI) above, namely, so-called nonionic compounds are preferred from the viewpoint that the solubility of unexposed areas in a developer containing an organic solvent is high to thereby suppress the occurrence of development defects. In particular, the compounds of general formulae (ZV) and (ZVI) above are more preferred.

Further, from the viewpoint of enhancing the efficiency of acid generation and acid strength, it is preferred for the acid generator (B) to have a structure capable of generating an acid containing a fluorine atom.

Specific examples of the photoacid generator (B) will be shown below, which however in no way limit the scope of the present invention.
One type of acid generator (B) may be used alone, or two or more types thereof may be used in combination. When two or more types of acid generators (B) are used in combination, it is preferred to use a combination of compounds that generate two types of organic acids being different from each other by two or more atoms with respect to the number of all atoms excluding hydrogen atoms.

For example, there can be mentioned a mode in which a compound with a structure capable of generating an acid containing a fluorine atom is combined with a compound not having such a structure from the viewpoint of enhancing the efficiency of acid generation and acid
strength.

The content of the photoacid generator (B) based on the total solids of the actinic-ray- or radiation-sensitive resin composition is preferably in the range of 0.1 to 20 mass%, more preferably 0.5 to 15 mass% and further more preferably 1 to 10 mass%.

Solvent

As a solvent which can be used for preparing the actinic-ray- or radiation-sensitive resin composition according to the present invention, an organic solvent such as an alkylene glycol monoalkyl ether carboxylate, an alkylene glycol monoalkyl ether, an alkyl lactate, an alkyl alkoxypropionate, a cyclolactone (preferably having 4 to 10 carbon atoms), an optionally cyclized monoketone compound (preferably having 4 to 10 carbon atoms), an alkylene carbonate, an alkyl alkoxyacetate and an alkyl pyruvate can be exemplified.

As specific examples of these solvents, there can be mentioned, for example, those described in section [0441] to [0445] of US Patent Application Publication No. 2008/0248425.

In the present invention, a mixed solvent consisting of a mixture of a solvent having a hydroxy group in its structure and a solvent having no hydroxy group may be used as the organic solvent.

As the solvent having a hydroxy group and the solvent having no hydroxy group, the compound
exemplified above can be used as appropriate. As the solvent having a hydroxy group, an alkylene glycol monoalkyl ether and ethyl lactate can be exemplified. Of these, propylene glycol monomethyl ether (PGME, also referred to as 1-methoxy-2-propanol) and ethyl lactate are more preferred. As the solvent having no hydroxy group, an alkylene glycol monoalkyl ether acetate, an alkylalkoxypropionate, a monoketone compound optionally with a ring structure, a cyclic lactone, and an alkyl acetate can be exemplified. Of these, a propylene glycol monomethyl ether acetate (PGMEA, also referred to as 1-methoxy-2-acetoxypropane), an ethyleoxypropionate, a 2-heptanone, a γ-butyl lactone, a cyclohexanone, or a butyl acetate is more preferred, and a propylene glycol monomethyl ether acetate, an ethyleoxypropionate, or a 2-heptanone is especially preferred.

When employing a mixed solvent consisting of a mixture of a solvent having a hydroxy group in its structure and a solvent having no hydroxy group, the mass ratio between them is preferably in the range of 1/99 to 99/1, more preferably 10/90 to 90/10, and further more preferably 20/80 to 60/40. The mixed solvent containing 50 mass% or more of a solvent having no hydroxyl group is especially preferred from the viewpoint of uniform applicability.

It is preferred for the solvent to contain
propylene glycol monomethyl ether acetate. A single solvent of propylene glycol monomethyl ether acetate or a mixed solvent of two or more solvents containing propylene glycol monomethyl ether acetate is more preferable.

(4) Basic compound

The actinic-ray- or radiation-sensitive resin composition of the present invention preferably contains a basic compound in order to reduce any performance change over time from exposure to bake.

As preferred basic compounds, the compounds having the structures represented by the following formulae (A) to (E) can be exemplified.

```
(A) \[\text{R}_2^01 \text{N} \text{R}_2^02\]

(B) \[\text{N} \text{C} = \text{N}\]

(C) \[\text{C} \text{N} = \text{C}\]

(D) \[\text{C} \text{N}\]

(E) \[\text{R}_2^04 \text{C} \text{N} \text{C} \text{R}_2^05\]
```

In the general formulae (A) and (E), \(\text{R}_{200}^0\) \(\text{R}_{201}\) and \(\text{R}_{202}\) each independently represents a hydrogen atom, an alkyl group (preferably having 1 to 20 carbon atoms), a cycloalkyl group (preferably having 3 to 20 carbon atoms) or an aryl group (having 6 to 20 carbon atoms).
carbon atoms). \( R_{201} \text{ and } R_{202} \) may be bonded to each other to form a ring. \( R_{203}, R_{204}, R_{205} \) and \( R_{206} \) each independently represents an alkyl group having 1 to 20 carbon atoms.

With respect to the above alkyl group, as a preferred substituted alkyl group, an aminoalkyl group having 1 to 20 carbon atoms, a hydroxyalkyl group having 1 to 20 carbon atoms, and a cyanoalkyl group having 1 to 20 carbon atoms can be exemplified. More preferably, the alkyl groups in the general formulae (A) and (E) are unsubstituted.

As preferred basic compounds, guanidine, aminopyrrolidine, pyrazole, pyrazoline, piperazine, aminomorpholine, aminoalkylmorpholine and piperidine can be exemplified. As more preferred compounds, those with an imidazole structure, a diazabicyclo structure, an onium hydroxide structure, an onium carboxylate structure, a trialkylamine structure, an aniline structure or a pyridine structure, alkylamine derivatives having a hydroxy group and/or an ether bond, and aniline derivatives having a hydroxy group and/or an ether bond can be exemplified.

As the compounds with an imidazole structure, imidazole, 2,4,5-triphenylimidazole, and benzimidazole can be exemplified. As the compounds with a diazabicyclo structure, 1,4-diazabicyclo [2,2,2]octane, 1,5-diazabicyclo [4,3,0] non-5-ene, and
1,8-diazabicyclo [5,4,0]undec-7-ene can be exemplified. As the compounds with an onium hydroxide structure, triarylsulfonyl onium hydroxide, phenacylsulfon onium hydroxide, sulfonium hydroxides having a 2-oxoalkyl group, such as triphenylsulfonyl onium hydroxide, tris (t-butylphenyl) sulfonium hydroxide, bis (t-butylphenyl) iodonium hydroxide, phenacylthiophenium hydroxide, and 2-oxopropylthiophenium hydroxide can be exemplified. As the compounds with an onium carboxylate structure, those having a carboxylate at the anion moiety of the compounds with an onium hydroxide structure, such as acetate, adamantane-1-carboxylate, and perfluoroalkyl carboxylate can be exemplified. As the compounds with a trialkylamine structure, tri (n-butyl) amine and tri (n-octyl) amine can be exemplified. As the aniline compounds, 2,6-diiisopropylaniline, N,N-dimethylaniline, N,N-dibutylaniline, and N,N-dihexylaniline can be exemplified. As the alkylamine derivatives having a hydroxy group and/or an ether bond, ethanolamine, diethanolamine, triethanolamine, and tris (methoxyethoxyethyl) amine can be exemplified. As the aniline derivatives having a hydroxy group and/or an ether bond, N,N-bis (hydroxyethyl) aniline can be exemplified.

As preferred basic compounds, an amine compound having a phenoxy group, an ammonium salt compound
having a phenoxy group, an amine compound having a sulfonic ester group, and an ammonium salt compound having a sulfonic ester group can further be exemplified.

In the amine compound having a phenoxy group, the ammonium salt compound having a phenoxy group, the amine compound having a sulfonic ester group, and the ammonium salt compound having a sulfonic ester group, it is preferred for at least one alkyl group to be bonded to a nitrogen atom. More preferably, an oxygen atom is contained in the chain of the alkyl group, thereby forming an oxyalkylene group. With respect to the number of oxyalkylene groups in each molecule, one or more is preferred, three to nine more preferred, and four to six further more preferred. Of these oxyalkylene groups, the groups of the formulae -CH2CH2O-, -CH(CH3)CH2O- and -CH2CH2CH2O- are especially preferred.

As specific examples of these compounds, there can be mentioned, for example, the compounds (Cl-1) to (C3-3) given as examples in section [0066] of US Patent Application Publication No. 2007/0224539 A.

The basic compound may be a compound whose basicity is increased by an action of an acid. As specific but not limited examples of these compounds, there can be mentioned, for example, the compounds described in JP-A-2007-298569 and JP-A-2009-199021.
The actinic-ray- or radiation-sensitive resin composition according to the present invention may or may not contain the basic compound. When the actinic-ray- or radiation-sensitive resin composition according to the present invention contains the basic compound, the total amount of basic compound used based on the solid contents of the actinic ray-sensitive or radiation-sensitive resin composition is generally in the range of 0.001 to 10 mass%, preferably 0.01 to 5 mass%.

With respect to the ratio between the acid generator and basic compound used in the composition, the ratio of acid generator to basic compound (molar ratio) is preferably in the range of 2.5 to 300. A molar ratio of 2.5 or higher is preferred from the viewpoint of sensitivity and resolving power. A molar ratio of 300 or below is preferred from the viewpoint of suppressing any resolving power drop due to pattern thickening over time until the baking treatment after exposure. The ratio of acid generator to basic compound (molar ratio) is more preferably in the range of 5.0 to 200, further more preferably 7.0 to 150.

[5] Surfactant

The actinic-ray- or radiation-sensitive resin composition according to the present invention may or may not contain a surfactant. When containing the surfactant, any one of a fluorinated and/or siliconized
surfactant (a fluorinated surfactant, a siliconized surfactant or a surfactant having both a fluorine atom and a silicon atom) or 2 or more types of these surfactants are preferably contained in the composition.

The actinic-ray- or radiation-sensitive resin composition according to the present invention when containing the above surfactant would, in the use of an exposure light source of 250 nm or below, especially 220 nm or below, realize favorable sensitivity and resolving power and produce a resist pattern with less adhesion and development defects.

As fluorinated and/or siliconized surfactants, there can be mentioned, for example, those described in section [0276] of US Patent Application Publication No. 2008/0248425. Further, as useful commercially available surfactants, fluorinated surfactants or siliconized surfactants, such as Eftop EF301 and EF303 (produced by Shin-Akita Kasei Co., Ltd.), Florad FC 430, 431 and 4430 (produced by Sumitomo 3M Ltd.), Megafac F171, F173, F176, F189, F113, F110, F177, F120 and R08 (produced by Dainippon Ink & Chemicals, Inc.), Surflon S-382, SC101, 102, 103, 104, 105, 106 and KH-20 (produced by Asahi Glass Co., Ltd.), Troy Sol S-366 (produced by Troy Chemical Co., Ltd.), GF-300 and GF-150 (produced by TOAGOSEI CO., LTD.), Sarfron S-393 (produced by SEIMI CHEMICAL CO., LTD.), Eftop EF121,
EF122A, EF122B, RF122C, EF125M, EF135M, EF351, EF352, EF801, EF802 and EF601 (produced by JEMCO INC.), PF636, PF656, PF6320 and PF6520 (produced by OMNOVA), and FTX-204G, 208G, 218G, 230G, 204D, 208D, 212D, 218D and 222D (produced by NEOS) can be exemplified. Further, polysiloxane polymer KP-341 (produced by Shin-Etsu Chemical Co., Ltd.) can be employed as the siliconized surfactant.

As the surfactant, besides the above publicly known surfactants, use can be made of a surfactant based on a polymer having a fluorinated aliphatic group derived from a fluorinated aliphatic compound, produced by a telomerization technique (also called a telomer process) or an oligomerization technique (also called an oligomer process). In particular, polymers each having a fluoroaliphatic group derived from such a fluoroaliphatic compound may be used as the surfactant. The fluorinated aliphatic compound can be synthesized by the process described in JP-A-2002-90991.

For example, as a surfactant described above, there can be mentioned Megafac F178, F-470, F-473, F-475, F-476 or F-472 (produced by Dainippon Ink & Chemicals, Inc.). Further, there can be mentioned a copolymer from an acrylate (or methacrylate) having a \( \text{C}_g \text{F}_3 \) group and a poly (oxyalkylene) acrylate (or methacrylate), a copolymer from an acrylate (or methacrylate) having a \( \text{C}_g \text{F}_3 \) group, poly (oxyethylene)
acrylate (or methacrylate) and poly (oxypropylene) acrylate (or methacrylate), or the like.

Further, use may be made of surfactants other than the fluorinated and/or siliconized surfactants, described in section [0280] of US Patent Application Publication No. 2008/0248425.

These surfactants may be used either individually or in combination.

The actinic-ray- or radiation-sensitive resin composition according to the present invention may or may not contain the surfactant. When the actinic-ray- or radiation-sensitive resin composition according to the present invention contains the surfactant, the total amount thereof used based on the total solids of the composition (with the exception of the solvent) is preferably in the range of 0.0001 to 2 mass%, more preferably 0.0005 to 1 mass%.

[6] Other additives

The actinic-ray- or radiation-sensitive resin composition according to the present invention may or may not further contain a carboxylic acid onium salt. As the carboxylic acid onium salt, these described in section [0605] to [0606] of US Patent Application Publication No. 2008/0187860 can be exemplified.

These carboxylic acid onium salts can be synthesized by reacting a sulfonium hydroxide, an iodonium hydroxide or an ammonium hydroxide and a
carboxylic acid with silver oxide in an appropriate solvent.

When the actinic-ray- or radiation-sensitive resin composition according to the present invention contains the carboxylic acid onium salt, the content ratio of carboxylic acid onium salt in the composition is generally in the range of 0.1 to 20 mass%, preferably 0.5 to 10 mass% and still more preferably 1 to 7 mass% based on the total solids of the composition.

The actinic-ray- or radiation-sensitive resin composition according to the present invention may further according to necessity contain a dye, a plasticizer, a photosensitizer, a light absorber, a resin soluble in alkali, a dissolution inhibiting compound, a compound capable of increasing the solubility in a developer (for example, a phenolic compound of 1000 or less molecular weight or a carboxylated alicyclic or aliphatic compound), etc.

The above phenolic compound of 1000 or less molecular weight can be easily synthesized by persons of ordinary skill in the art to which the present invention pertains while consulting the processes described in, for example, JP-As 4-122938 and 2-28531, USP 4,916,210 and EP 219294.

As the carboxylated alicyclic or aliphatic compound, there can be mentioned, for example, a carboxylic acid derivative of steroid structure such as
cholic acid, deoxycholic acid or lithocholic acid, an
adamantanecarboxylic acid derivative,
adamantanedicarboxylic acid, cyclohexanecarboxylic
acid, cyclohexanedicarboxylic acid or the like. These
are however nonlimiting.

From the viewpoint of enhancement of resolving
power, it is preferred for the actinic-ray- or
radiation-sensitive resin composition of the present
invention to be used with a coating thickness of 30 to
250 nm. More preferably, the actinic-ray- or
radiation-sensitive resin composition is used with a
coating thickness of 30 to 200 nm. This coating
thickness can be attained by setting the solid content
of the composition within an appropriate range so as to
cause the composition to have an appropriate viscosity,
thereby improving the applicability and film forming
property.

The solid concentration of the actinic-ray- or
radiation-sensitive resin composition according to the
present invention is generally in the range of 1.0 to
15 mass%, preferably 2.5 to 13 mass% and more
preferably 3.0 to 12 mass%. The resist solution can be
uniformly applied onto substrates by regulating the
solid concentration to this range. Further, a resist
pattern exhibiting a high resolution and a rectangular
profile and excelling in etching resistance can be
formed. Although the reason therefor is not
necessarily apparent, it is presumed that very possibly, the aggregation of materials, especially photoacid generators, in the resist solution can be inhibited by regulating the solid concentration to 10 mass% or below, preferably 5.7 mass% or below, so that a uniform resist film can be formed.

The term "solid concentration" means the percentage of the weight of non-solvent resist components based on the total weight of the actinic-ray- or radiation-sensitive resin composition.

The resist film of the present invention is a film formed from the above actinic-ray- or radiation-sensitive resin composition. For example, it is a film formed by applying the actinic-ray- or radiation-sensitive resin composition onto a substrate.

The actinic-ray- or radiation-sensitive resin composition according to the present invention is used in such a manner that the above-mentioned components are dissolved in a given organic solvent, preferably the above-mentioned mixed solvent, and filtered and applied onto a given support (substrate). The filter medium for use in the filtration is preferably one made of a polytetrafluoroethylene, polyethylene or nylon that has a pore size of 0.1 µm or less, preferably 0.05 µm or less and more preferably 0.03 µm or less. In the filtration, as described in, for example, JP-A-2002-62667, a cyclic filtration may be carried out, or
two or more types of filters may be connected in series or parallel. Moreover, the composition may be filtered two or more times. Further, the composition may be deaerated prior to or after the filtration.

Examples

The present invention will be described in greater detail below by way of its examples. However, the gist of the present invention is in no way limited to these examples.

<Synthetic Example (synthesis of resin P-1)>

In a nitrogen gas stream, 51.3 parts by mass of cyclohexanone was heated at 80°C. While agitating the liquid, a solution comprised of a mixture of 27.8 parts by mass of monomer of structural formula A below, 21.0 parts by mass of monomer of structural formula B below, 95.2 parts by mass of cyclohexanone and 1.73 parts by mass of dimethyl 2,2'-azobisisobutyrate [V601, produced by Wako Pure Chemical Industries, Ltd.] was dropped thereinto over a period of four hours. After the completion of the dropping, the mixture was further agitated at 80°C for two hours. The thus obtained reaction liquid was allowed to stand still to cool, re-precipitated in a large volume of hexane/ethyl acetate (mass ratio: 8/2) and filtered. The thus obtained solid was dried in a vacuum, thereby obtaining 45.2 parts by mass of resin P-1 according to the present invention.
With respect to the obtained resin, it was found by GPC (carrier: tetrahydrofuran (THF)) that the weight average molecular weight (\(M_w\) polystyrene-equivalent) was 15,000 and the polydispersity index (\(M_w/M_n\)) was 1.72. The component ratio determined by \(^{13}\text{C}\)-NMR was 50/50.

Resins P-2 to P-31 were synthesized in the same manner as in the synthesis of resin P-1. The structures of synthesized resins P-1 to P-31 are shown below.
With respect to each of the above synthesized resins, the individual repeating unit ratios, weight average molecular weight ($M_w$) and polydispersity index ($M_w/M_n$) are given in Table 1 below. The left to right order of listing of numerics indicating individual repeating unit ratios of Table 1 corresponds to that of the arrangement of individual repeating unit structures of resins P-1 to P-31 shown above.
Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Component ratio (mol%)</th>
<th>Mw</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>50 50 - - -</td>
<td>15000</td>
<td>1.72</td>
</tr>
<tr>
<td>P-2</td>
<td>50 15 35 - -</td>
<td>16200</td>
<td>1.74</td>
</tr>
<tr>
<td>P-3</td>
<td>50 40 10 - -</td>
<td>14800</td>
<td>1.71</td>
</tr>
<tr>
<td>P-4</td>
<td>55 40 5 - -</td>
<td>9100</td>
<td>1.63</td>
</tr>
<tr>
<td>P-5</td>
<td>50 40 10 - -</td>
<td>17500</td>
<td>1.76</td>
</tr>
<tr>
<td>P-6</td>
<td>45 25 15 15 -</td>
<td>15300</td>
<td>1.75</td>
</tr>
<tr>
<td>P-7</td>
<td>45 50 5 - -</td>
<td>16700</td>
<td>1.78</td>
</tr>
<tr>
<td>P-8</td>
<td>50 45 5 - -</td>
<td>23900</td>
<td>1.93</td>
</tr>
<tr>
<td>P-9</td>
<td>40 50 10 - -</td>
<td>28400</td>
<td>2.07</td>
</tr>
<tr>
<td>P-10</td>
<td>40 10 50 - -</td>
<td>18600</td>
<td>1.80</td>
</tr>
<tr>
<td>P-11</td>
<td>55 40 5 - -</td>
<td>19200</td>
<td>1.86</td>
</tr>
<tr>
<td>P-12</td>
<td>45 50 5 - -</td>
<td>25000</td>
<td>1.99</td>
</tr>
<tr>
<td>P-13</td>
<td>45 30 20 5 -</td>
<td>28700</td>
<td>2.04</td>
</tr>
<tr>
<td>P-14</td>
<td>30 10 50 10 -</td>
<td>27300</td>
<td>2.06</td>
</tr>
<tr>
<td>P-15</td>
<td>30 5 30 30 5</td>
<td>30100</td>
<td>2.09</td>
</tr>
<tr>
<td>P-16</td>
<td>30 5 25 30 10</td>
<td>29400</td>
<td>2.07</td>
</tr>
<tr>
<td>P-17</td>
<td>40 30 20 10 -</td>
<td>24400</td>
<td>1.97</td>
</tr>
<tr>
<td>P-18</td>
<td>30 30 35 5 -</td>
<td>26200</td>
<td>1.95</td>
</tr>
<tr>
<td>P-19</td>
<td>40 45 10 5 -</td>
<td>21400</td>
<td>1.84</td>
</tr>
<tr>
<td>P-20</td>
<td>50 45 5 - -</td>
<td>13900</td>
<td>1.68</td>
</tr>
<tr>
<td>P-21</td>
<td>35 55 10 - -</td>
<td>11100</td>
<td>1.70</td>
</tr>
<tr>
<td>P-22</td>
<td>40 40 20 - -</td>
<td>30800</td>
<td>2.11</td>
</tr>
<tr>
<td>P-23</td>
<td>50 40 10 - -</td>
<td>24700</td>
<td>1.93</td>
</tr>
<tr>
<td>P-24</td>
<td>45 25 25 5 -</td>
<td>25100</td>
<td>1.97</td>
</tr>
<tr>
<td>P-25</td>
<td>50 40 10 - -</td>
<td>21000</td>
<td>1.82</td>
</tr>
<tr>
<td>P-26</td>
<td>40 55 5 - -</td>
<td>18600</td>
<td>1.81</td>
</tr>
<tr>
<td>P-27</td>
<td>40 45 10 5 -</td>
<td>12300</td>
<td>1.75</td>
</tr>
<tr>
<td>P-28</td>
<td>45 10 40 5 -</td>
<td>20900</td>
<td>1.83</td>
</tr>
<tr>
<td>P-29</td>
<td>40 40 10 10 -</td>
<td>28500</td>
<td>1.96</td>
</tr>
<tr>
<td>P-30</td>
<td>45 50 5 - -</td>
<td>26600</td>
<td>2.06</td>
</tr>
<tr>
<td>P-31</td>
<td>35 45 10 10 -</td>
<td>13000</td>
<td>1.69</td>
</tr>
</tbody>
</table>

<Acid generator>

The following compounds (PAG-1) to (PAG-8) were
used as acid generators.

The following compounds (N-1) to (N-4) were used as basic compounds.
The surfactant for use was appropriately selected from among the following surfactants (W-1) to (W-6).

W-1: Megafac F176 (produced by Dainippon Ink & Chemicals, Inc., fluorinated),

W-2: Megafac R08 (produced by Dainippon Ink & Chemicals, Inc., fluorinated and siliconized),

W-3: polysiloxane polymer KP-341 (produced by Shin-Etsu Chemical Co., Ltd., siliconized),

W-4: Troy Sol S-366 (produced by Troy Chemical Co., Ltd.),

W-5: KH-20 (produced by Asahi Glass Co., Ltd.), and

W-6: PolyFox PF-6320 (produced by OMNOVA SOLUTIONS, INC., fluorinated).

The solvent for use was appropriately selected
from among the following solvents SL-1 to SL-8.

(Group a)
SL-1: propylene glycol monomethyl ether acetate (PGMEA),

SL-2: propylene glycol monomethyl ether propionate, and
SL-3: 2-heptanone.

(Group b)
SL-4: ethyl lactate,

SL-5: propylene glycol monomethyl ether (PGME), and
SL-6: cyclohexanone.

(Group c)
SL-7: γ-butyrolactone, and
SL-8: propylene carbonate.

<Preparation of resist>
The actinic-ray- or radiation-sensitive resin compositions (resist compositions) for use in Examples 1 to 32 were prepared by dissolving individual components indicated in Table 2 below in solvents indicated in the same table in a solid content of 5.10 mass% and passing the solutions through a polyethylene filter of 0.1 μm pore size.
<table>
<thead>
<tr>
<th>Example</th>
<th>Compound (B)</th>
<th>Resin</th>
<th>Basic compound</th>
<th>Mass ratio</th>
<th>Solvent</th>
<th>Surface ant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 2</td>
<td>P-1 10</td>
<td>PAG-5</td>
<td>N-1/N-4</td>
<td>0.003 0.03</td>
<td>SL-1/SL-5</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 3</td>
<td>P-2 10</td>
<td>PAG-1</td>
<td>N-4</td>
<td>0.003 0.05</td>
<td>SL-1/SL-5</td>
<td>W-3</td>
</tr>
<tr>
<td>Example 4</td>
<td>P-3 10</td>
<td>PAG-5</td>
<td>N-4</td>
<td>0.003 0.05</td>
<td>SL-1/SL-5</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 5</td>
<td>P-4 10</td>
<td>PAG-6</td>
<td>N-2</td>
<td>0.003 0.07</td>
<td>SL-1/SL-5</td>
<td>W-2</td>
</tr>
<tr>
<td>Example 6</td>
<td>P-5 10</td>
<td>PAG-2</td>
<td>N-3</td>
<td>0.003 0.05</td>
<td>SL-1/SL-2</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 7</td>
<td>P-6 10</td>
<td>PAG-6</td>
<td>N-4</td>
<td>0.003 0.05</td>
<td>SL-1/SL-5</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 8</td>
<td>P-7 10</td>
<td>PAG-3</td>
<td>N-2</td>
<td>0.003 0.05</td>
<td>SL-1/SL-2</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 9</td>
<td>P-8 10</td>
<td>PAG-3</td>
<td>N-1</td>
<td>0.003 0.05</td>
<td>SL-1/SL-2</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 10</td>
<td>P-9 10</td>
<td>PAG-2</td>
<td>N-1</td>
<td>0.003 0.05</td>
<td>SL-1/SL-3</td>
<td>W-1</td>
</tr>
<tr>
<td>Example 11</td>
<td>P-11 10</td>
<td>PAG-2</td>
<td>N-1</td>
<td>0.003 0.05</td>
<td>SL-1/SL-3</td>
<td>W-1</td>
</tr>
<tr>
<td>Example</td>
<td>Resin (g)</td>
<td>Compound (B)</td>
<td>(g)</td>
<td>Basic compound (g)</td>
<td>Solvent</td>
<td>Mass ratio</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>--------------</td>
<td>-----</td>
<td>--------------------</td>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>Example 12</td>
<td>P-12 10</td>
<td>PAG-1/PAG-3</td>
<td>0.57</td>
<td>N-3 0.07</td>
<td>SL-1/SL-5</td>
<td>60/40</td>
</tr>
<tr>
<td>Example 13</td>
<td>P-13 10</td>
<td>PAG-3</td>
<td>0.86</td>
<td>N-1 0.04</td>
<td>SL-1/SL-5</td>
<td>70/30</td>
</tr>
<tr>
<td>Example 14</td>
<td>P-14 10</td>
<td>PAG-8</td>
<td>1.08</td>
<td>N-1 0.05</td>
<td>SL-1/SL-8</td>
<td>90/10</td>
</tr>
<tr>
<td>Example 15</td>
<td>P-15 10</td>
<td>PAG-3</td>
<td>1.03</td>
<td>N-4 0.05</td>
<td>SL-1</td>
<td>100</td>
</tr>
<tr>
<td>Example 16</td>
<td>P-16 10</td>
<td>PAG-3</td>
<td>0.86</td>
<td>N-1 0.05</td>
<td>SL-1/SL-5</td>
<td>60/40</td>
</tr>
<tr>
<td>Example 17</td>
<td>P-17 10</td>
<td>PAG-5</td>
<td>0.90</td>
<td>N-1/N-2 0.03/0.02</td>
<td>SL-1/SL-5</td>
<td>80/20</td>
</tr>
<tr>
<td>Example 18</td>
<td>P-18 10</td>
<td>PAG-3</td>
<td>0.89</td>
<td>N-1 0.04</td>
<td>SL-1/SL-5</td>
<td>60/40</td>
</tr>
<tr>
<td>Example 19</td>
<td>P-19 10</td>
<td>PAG-4</td>
<td>0.72</td>
<td>N-3 0.07</td>
<td>SL-1/SL-5</td>
<td>80/20</td>
</tr>
<tr>
<td>Example 20</td>
<td>P-20 10</td>
<td>PAG-7</td>
<td>1.11</td>
<td>N-1 0.05</td>
<td>SL-1/SL-5</td>
<td>60/40</td>
</tr>
<tr>
<td>Example 21</td>
<td>P-21 10</td>
<td>PAG-1</td>
<td>0.95</td>
<td>N-2 0.04</td>
<td>SL-1/SL-4</td>
<td>90/10</td>
</tr>
<tr>
<td>Example 22</td>
<td>P-22 10</td>
<td>PAG-2</td>
<td>0.71</td>
<td>N-1 0.05</td>
<td>SL-1/SL-5</td>
<td>60/40</td>
</tr>
<tr>
<td>Example</td>
<td>Compound (g)</td>
<td>Basic compound (g)</td>
<td>Solvent</td>
<td>Mass ratio</td>
<td>Surface tension</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td>-------------------</td>
<td>---------</td>
<td>------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>P-23 10</td>
<td>N-3 0.90</td>
<td>SL-1/SL-7 0.07</td>
<td>W-1 70/30</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>P-24 10</td>
<td>N-3 0.86</td>
<td>SL-1/SL-7 0.07</td>
<td>W-6 60/40</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>P-25 10</td>
<td>N-3 1.14</td>
<td>SL-1/SL-5 0.05</td>
<td>W-3 70/30</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>P-26 10</td>
<td>N-3 0.90</td>
<td>SL-1/SL-7 0.07</td>
<td>W-1 70/30</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>P-27 10</td>
<td>N-3 1.08</td>
<td>SL-1/SL-5 0.03</td>
<td>W-6 60/40</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>P-28 10</td>
<td>N-3 1.06</td>
<td>SL-1/SL-5 0.03</td>
<td>W-1 70/30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>P-29 10</td>
<td>N-3 0.90</td>
<td>SL-1/SL-5 0.04</td>
<td>W-2 60/40</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>P-30 10</td>
<td>N-3 1.08</td>
<td>SL-1/SL-5 0.07</td>
<td>W-2 none</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>P-31 10</td>
<td>N-2 0.89</td>
<td>SL-1/SL-4 0.05</td>
<td>W-1 70/20</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>P-1 6/4</td>
<td>N-2 0.89</td>
<td>SL-7 0.05</td>
<td>W-1 /10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2 (cont.)**
A substrate with an uneven surface was produced for the evaluation of the above prepared resist compositions. The characteristics of pattern formation of each of the resist compositions on the uneven-surface substrate were evaluated. The evaluation method will be described below with reference to FIG. 1.

<Fabrication of substrate with uneven surface>

Referring to FIG. IB, a positive resist composition 3 (FAiRS-G104: produced by FUJIFILM Electronic Materials Co., Ltd.) was applied onto an Si substrate 1 provided on its surface with a 500 nm thick SiC<2 coating 2 as shown in FIG. 1A in a thickness of 200 nm, and baked at 100 °C for 60 seconds. The baked positive resist film was exposed through a mask provided with 220 nm wide line patterns and 180 nm spaces to light by means of an ArF excimer laser (PAS5500/1100, manufactured by ASML), and baked at 95°C for 60 seconds. The thus exposed wafer was developed with a 2.38 mass% aqueous tetramethylammonium hydroxide solution for 30 seconds, rinsed with pure water and spin dried. As a result, a resist pattern with 220 line portions and 180 nm space portions was obtained (FIG. 1C).

Etching treatment using CF4 gas by means of an etching apparatus (NLD-800, manufactured by ULVAC) was performed on the wafer provided with the above pattern
for 30 seconds, so that the SiO2 coating 2 was etched to a depth of 100 nm (FIG. ID). The wafer after the etching was dipped in an alkali developer (TMAH: 2.38%) for 60 seconds, thereby removing the resist composition. Thus, a substrate with an uneven surface as shown in (FIG. IE) was obtained.

<Evaluation of characteristics of pattern formation on substrate with uneven surface>

Each of the above prepared resist compositions 4 of Examples 1 to 32 was applied onto the above obtained substrate with an uneven surface in a thickness of 150 nm on protrudent portions (FIG. IF), and prebaked (PB) at 100°C for 60 seconds. The prebaked resist film was exposed through a mask provided with 400 nm wide line patterns and 400 nm spaces to light by means of a KrF excimer laser (PAS5500/850, manufactured by ASML), and post-exposure baked (PEB) at 110°C for 60 seconds. The thus obtained exposed wafer was developed with an organic solvent (butyl acetate) for 30 seconds, and rotated at a rotating speed of 4000 rpm for 30 seconds. In this manner, patterning as shown in FIG. 1G was attempted.

As a result, it was found that when the compositions according to the present invention were used, in any of Examples 1 to 32, the desired patterning by KrF exposure was realized on the substrate with an uneven surface.
Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

Reference Symbol List

1: Si substrate, 2: SiO2 coating, 3: Positive resist composition, 4: Resist composition of working example
1. A method of forming a pattern, comprising:

(i) forming a film from an actinic-ray- or radiation-sensitive resin composition comprising a resin (P) containing at least one repeating unit (a) represented by at least one of general formula (I) and (II) below and at least one repeating unit (b) represented by at least one of general formulae (III), (IV) and (V) below and further comprising a compound (B) that generates an acid when exposed to actinic rays or radiation;

(ii) exposing the film to light by means of a KrF excimer laser; and

(iii) developing the exposed film with a developer containing an organic solvent, thereby forming a negative pattern,
each of $R_{11}$, $R_{21}$, $R_{31}$, $R_{41}$ and $R_{51}$ independently represents a hydrogen atom or a methyl group;

$R_{12}$ represents a hydrogen atom or a $-\text{COOCH}_3$ group;

$X$ represents a methylene group or an oxygen atom;

each of $R_{32}$, $R_{42}$ and $R_{52}$ independently represents an alkyl group having 1 to 4 carbon atoms;

$m$ is 0 or 1; and

$n$ is 1 or 2.

2. The method according to claim 1, wherein the repeating unit (a) comprises at least one repeating unit represented by the general formula (I) and the repeating unit (b) comprises at least one repeating unit represented by the general formula (IV).

3. The method according to claim 1 or 2, wherein the organic solvent contained in the developer is at least one solvent selected from the group consisting of a ketone solvent, an ester solvent, an alcohol solvent, an amide solvent, an ether solvent and a hydrocarbon solvent.

4. The method according to any one of claims 1 to 3, further comprising, to be performed after the development of the film with the developer, (iv) rinsing the film with a rinse liquid containing an organic solvent.

5. The method according to any one of claims 1 to 4, wherein the negative pattern is formed on an uneven-surface substrate.
6. An actinic-ray- or radiation-sensitive resin composition for use in the method according to any one of claims 1 to 5.

7. An actinic-ray- or radiation-sensitive film formed from the actinic-ray- or radiation-sensitive resin composition according to claim 6.

8. A process for manufacturing an electronic device comprising the method according to any one of claims 1 to 5.

9. An electronic device manufactured by the process according to claim 8.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. G03F7/038 (2006.01) i, C08F220/18 (2006.01) i, C08F220/28 (2006.01) i, G03F7/039 (2006.01) i, G03F7/32 (2006.01) i, H01L21/027 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. G03F7/038, C08F220/18, C08F220/28, G03F7/039, G03F7/32, H01L21/027

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

- Published examined utility model applications of Japan 1922-1996
- Published unexamined utility model applications of Japan 1971-2012
- Registered utility model specifications of Japan 1996-2012
- Published registered utility model applications of Japan 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

Further documents are listed in the continuation of Box C.

Date of the actual completion of the international search: 20.07.2012
Date of mailing of the international search report: 31.07.2012

Name and mailing address of the ISA/JP

Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer
Takayuki Sotokawa
Telephone No. +81-3-3581-1101 Ext. 3231