substrate is required. In the patterning used for ion implantation, one of tasks difficult to solve is the problem of scum on the substrate, which is generated after development due to bad removability of the film formed from the resist composition. In the case of developing the resist film with an aqueous alkali developer, the exposed area of the resist film is dissolved with the developer and therefore, for allowing no remaining of a resist film residue, sufficient light must be applied to the bottom of the resist film, but when such light is applied, the effect of reflection by the substrate becomes strong, and the resist film in the unexposed area, which should remain as a pattern, is exposed to the reflected light, causing a problem that the bottom of the pattern falls off. Accordingly, when the resist film is developed with an aqueous alkali developer, it is difficult to solve the problem of scum on the substrate while keeping a good pattern profile. Particularly, in the patterning on the stepped substrate above or the patterning without forming a bottom anti-reflection coating on a substrate, the effect of light reflection by the substrate becomes strong, and the problem of scum generated on the substrate after development is serious.

Summary of Invention

~~An object~~Embodiments of the present invention ~~is to solve the above-described problems and, for~~ disclose method for stably forming a highly precise fine pattern and thereby producing a high-integration and high-precision electronic device, provide a negative pattern forming method comprising forming a film with a film thickness of 200 nm or more from a chemical amplification resist composition, and exposing and developing the film, wherein the removability of the film is improved to reduce scum generated on the substrate after development and at the same time, an excellent performance is exhibited in terms of scum defect reduction and resolution; and a resist pattern formed by the negative pattern forming method.

~~The present invention includes the following configurations, and the above-described object of the present invention is attained by these configurations.~~

~~[1] A negative pattern forming method, comprising:~~

~~(i) forming a film having a film thickness of 200 nm or more from a chemical amplification resist composition containing (A) a resin capable of increasing a polarity of the resin (A) by an action of an acid to decrease a solubility of the resin (A) for a developer containing one or more organic solvents, (B) a compound capable of generating an acid upon irradiation with an actinic ray or radiation, and (C) a solvent;~~

(ii) exposing the film, so as to form an exposed film; and

(iii) developing the exposed film with a developer containing one or more organic solvents.

[2] The negative pattern forming method as described in [1] above,

wherein the film formed from the chemical amplification resist composition is formed on a substrate not coated with a bottom anti-reflection coating.

[3] The negative pattern forming method as described in [2] above,

wherein the substrate not coated with a bottom anti-reflection coating is a stepped substrate having a step of 10 nm or more in height.

[4] The negative pattern forming method as described in any one of [1] to [3] above,

wherein the resin (A) contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group, in an amount of 40 mol% or more based on all repeating units in the resin (A).

[5] The negative pattern forming method as described in any one of [1] to [4] above,

wherein the resin (A) has a weight average molecular weight of 5,000 or more.

[6] The negative pattern forming method as described in any one of [1] to [5] above,

wherein the developer containing one or more organic solvents contains at least one kind of an organic solvent selected from the group consisting of a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, an amide-based solvent and an ether-based solvent.

[7] The negative pattern forming method as described in any one of [1] to [6] above, further comprising:

(iv) performing rinsing by using a rinsing solution containing one or more organic solvents.

[8] The negative pattern forming method as described in any one of [1] to [7] above,

wherein the exposing of the film in the step (ii) is exposure to an ArF excimer laser.

[9] The negative pattern forming method as described in any one of [1] to [8] above,

~~wherein the film thickness of the film formed from the chemical amplification resist composition is 600 nm or less.~~

~~[10] A resist pattern formed by the negative pattern forming method described in any one of [1] to [9] above.~~

~~[11] A manufacturing method of an electronic device, comprising:~~

~~the negative pattern forming method described in any one of [1] to [9] above.~~

~~[12] The electronic device manufactured by the manufacturing method of the electronic device described in [11] above.~~

~~The present invention preferably further includes the following configurations.~~

~~[13] A chemical amplification resist composition used for the negative pattern forming method described in any one of [1] to [9] above.~~

~~[14] The chemical amplification resist composition as described in [13] above, which is used for ion implantation.~~

~~[15] A resist film formed from the chemical amplification resist composition described in [13] or [14] above.~~

~~[16] The negative pattern forming method as described in any one of [1] to [9] above,~~

~~wherein a water content ratio as the entire developer in the developer containing one or more organic solvents is less than 10 mass%.~~

~~[17] The negative pattern forming method as described in any one of [1] to [9] and [16] above,~~

~~wherein the developer containing one or more organic solvents contains substantially no water.~~

According to a first aspect of the present invention, there is provided a negative pattern forming method, comprising: forming a film having a film thickness of 200 nm or more from a chemical amplification resist composition containing a resin capable of increasing a polarity of the resin by an action of an acid to decrease a solubility of the resin for a developer containing one or more organic solvents, a compound capable of generating an acid upon irradiation with an actinic ray or radiation, and a solvent; exposing the film, so as to form an exposed film; and developing the exposed film with a developer containing one or more organic solvents, wherein the film formed from the chemical amplification resist composition is formed on a substrate not coated with a bottom anti-reflection coating, and the

substrate not coated with a bottom anti-reflection coating is a stepped substrate having a step of 10 nm or more in height.

In an embodiment, the resin contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group, in an amount of 40 mol% or more based on all repeating units in the resin.

According to a second aspect of the present invention, there is provided a negative pattern forming method, comprising: forming a film having a film thickness of 200 nm or more from a chemical amplification resist composition containing a resin capable of increasing a polarity of the resin by an action of an acid to decrease a solubility of the resin for a developer containing one or more organic solvents, a compound capable of generating an acid upon irradiation with an actinic ray or radiation, and a solvent; exposing the film, so as to form an exposed film; and developing the exposed film with a developer containing one or more organic solvents, wherein the resin contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group, in an amount of from 45 mol% to 95 mol% based on all repeating units in the resin.

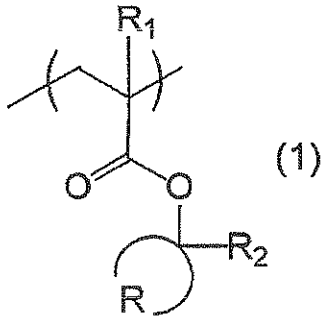
In an embodiment, the film formed from the chemical amplification resist composition is formed on a substrate not coated with a bottom anti-reflection coating.

In an embodiment, the substrate not coated with a bottom anti-reflection coating is a stepped substrate having a step of 10 nm or more in height.

In an embodiment, a content of the repeating unit has a group capable of decomposing by an action of an acid to produce a polar group is 50 mol% or more based on all repeating units in the resin.

In an embodiment, a content of the repeating unit has a group capable of decomposing by an action of an acid to produce a polar group is 55 mol% or more based on all repeating units in the resin.

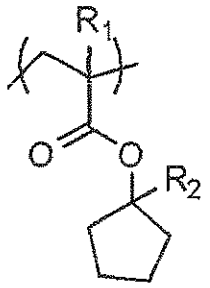
In an embodiment, the resin contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group and the repeating unit is represented by the following formula (1):



(1)

in formula (1), R_1 represents a hydrogen atom, a methyl group which may have a substituent, or a group represented by $-CH_2-R_9$, wherein R_9 represents a hydroxyl group or a monovalent organic group, R_2 represents an alkyl group or a cycloalkyl group, and R represents an atomic group necessary for forming a monocyclic alicyclic structure together with the carbon atom.

In an embodiment, the repeating unit has a group capable of decomposing by an action of an acid to produce a polar group is a repeating unit represented by the following formula (1-a):



(1-a)

in the formula (1-a), R_1 represents a hydrogen atom, a methyl group which may have a substituent, or a group represented by $-CH_2-R_9$, wherein R_9 represents a hydroxyl group or a monovalent organic group, R_2 represents an alkyl group or a cycloalkyl group.

In an embodiment, the resin contains a repeating unit has a group capable of decomposing by an action of an acid to produce an alcoholic hydroxyl group as a polar group.

In an embodiment, a content of an aromatic group-containing repeating unit in the resin is 5 mol% or less based on all repeating units in the resin.

In an embodiment, the resin has a weight average molecular weight of 5,000 or more.

In an embodiment, the developer containing one or more organic solvents contains at least one kind of an organic solvent selected from the group consisting of a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, an amide-based solvent and an ether-based solvent.

In an embodiment, the one or more organic solvents in the developer is butyl acetate.

In an embodiment, a water content ratio as the entire developer in the developer containing one or more organic solvents is less than 10 mass%.

In an embodiment, the developer containing one or more organic solvents contains substantially no water.

In an embodiment, the above negative pattern forming method further comprises performing rinsing by using a rinsing solution containing one or more organic solvents.

In an embodiment, the exposing of the film in the step is exposure to an ArF excimer laser.

In an embodiment, the film thickness of the film formed from the chemical amplification resist composition is 600 nm or less.

According to a third aspect of the present invention, there is provided a resist pattern formed by the above negative pattern forming method.

Description of Embodiments

The mode for carrying out the present invention is described below.

In the description of the present invention, when a group (atomic group) is denoted without specifying whether substituted or unsubstituted, the group includes both a group having no substituent and a group having a substituent. For example, "an alkyl group" includes not only an alkyl group having no substituent (unsubstituted alkyl group) but also an alkyl group having a substituent (substituted alkyl group).

In the description of the present invention, the term "actinic ray" or "radiation"

CLAIMS

1. A negative pattern forming method, comprising:

(i) forming a film having a film thickness of 200 nm or more from a chemical amplification resist composition containing (A) a resin capable of increasing a polarity of the resin (A) by an action of an acid to decrease a solubility of the resin (A) for a developer containing one or more organic solvents, (B) a compound capable of generating an acid upon irradiation with an actinic ray or radiation, and (C) a solvent;

(ii) exposing the film, so as to form an exposed film; and

(iii) developing the exposed film with a developer containing one or more organic solvents.

2. The negative pattern forming method according to claim 1,

wherein the film formed from the chemical amplification resist composition is formed on a substrate not coated with a bottom anti-reflection coating.

3. The negative pattern forming method according to claim 2,

wherein the substrate not coated with a bottom anti-reflection coating is a stepped substrate having a step of 10 nm or more in height.

4. The negative pattern forming method according to any one of claims 1 to 3,

wherein the resin (A) contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group, in an amount of 40 mol% or more based on all repeating units in the resin (A).

5. The negative pattern forming method according to any one of claims 1 to 4,

wherein the resin (A) has a weight average molecular weight of 5,000 or more.

6. The negative pattern forming method according to any one of claims 1 to 5,

wherein the developer containing one or more organic solvents contains at least one kind of an organic solvent selected from the group consisting of a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, an amide-based solvent and an ether-based

solvent.

7. The negative pattern forming method according to any one of claims 1 to 6, further comprising:

(iv) performing rinsing by using a rinsing solution containing one or more organic solvents.

8. The negative pattern forming method according to any one of claims 1 to 7,

wherein the exposing of the film in the step (ii) is exposure to an ArF excimer laser.

9. The negative pattern forming method according to any one of claims 1 to 8,

wherein the film thickness of the film formed from the chemical amplification resist composition is 600 nm or less.

10. A resist pattern formed by the negative pattern forming method claimed in any one of claims 1 to 9.

11. A manufacturing method of an electronic device, comprising:

the negative pattern forming method claimed in any one of claims 1 to 9.

12. An electronic device manufactured by the manufacturing method of an electronic device claimed in claim 11.

CLAIMS:

1. A negative pattern forming method, comprising:

(i) forming a film having a film thickness of 200 nm or more from a chemical amplification resist composition containing (A) a resin capable of increasing a polarity of the resin (A) by an action of an acid to decrease a solubility of the resin (A) for a developer containing one or more organic solvents, (B) a compound capable of generating an acid upon irradiation with an actinic ray or radiation, and (C) a solvent;

(ii) exposing the film, so as to form an exposed film; and

(iii) developing the exposed film with a developer containing one or more organic solvents,

wherein the film formed from the chemical amplification resist composition is formed on a substrate not coated with a bottom anti-reflection coating, and

the substrate not coated with a bottom anti-reflection coating is a stepped substrate having a step of 10 nm or more in height.

2. The negative pattern forming method according to claim 1,

wherein the resin (A) contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group, in an amount of 40 mol% or more based on all repeating units in the resin (A).

3. A negative pattern forming method, comprising:

(i) forming a film having a film thickness of 200 nm or more from a chemical amplification resist composition containing (A) a resin capable of increasing a polarity of the resin (A) by an action of an acid to decrease a solubility of the resin (A) for a developer containing one or more organic solvents, (B) a compound capable of generating an acid upon irradiation with an actinic ray or radiation, and (C) a solvent;

(ii) exposing the film, so as to form an exposed film; and

(iii) developing the exposed film with a developer containing one or more organic solvents,

wherein the resin (A) contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group, in an amount of from 45 mol% to 95 mol% based on all repeating units in the resin (A).

4. The negative pattern forming method according to claim 3,

wherein the film formed from the chemical amplification resist composition is formed on a substrate not coated with a bottom anti-reflection coating.

5. The negative pattern forming method according to claim 4,

wherein the substrate not coated with a bottom anti-reflection coating is a stepped substrate having a step of 10 nm or more in height.

6. The negative pattern forming method according to any one of claims 2 to 5,

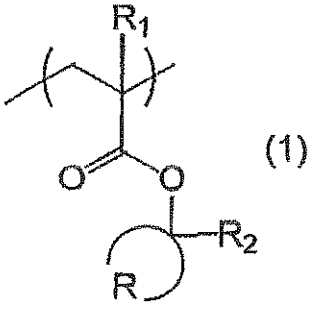
wherein a content of the repeating unit having a group capable of decomposing by an action of an acid to produce a polar group is 50 mol% or more based on all repeating units in the resin (A).

7. The negative pattern forming method according to claims 6,

wherein a content of the repeating unit having a group capable of decomposing by an action of an acid to produce a polar group is 55 mol% or more based on all repeating units in the resin (A).

8. The negative pattern forming method according to any one of claims 1 to 7,

wherein the resin (A) contains a repeating unit having a group capable of decomposing by an action of an acid to produce a polar group and the repeating unit is represented by the following formula (1):



(1)

in formula (1),

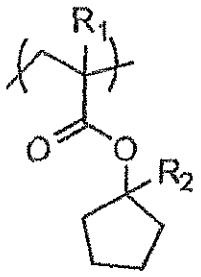
R_1 represents a hydrogen atom, a methyl group which may have a substituent, or a group represented by $-CH_2-R_9$, wherein R_9 represents a hydroxyl group or a monovalent organic group,

R_2 represents an alkyl group or a cycloalkyl group, and

R represents an atomic group necessary for forming a monocyclic alicyclic structure together with the carbon atom.

9. The negative pattern forming method according to claim 8,

wherein the repeating unit having a group capable of decomposing by an action of an acid to produce a polar group is a repeating unit represented by the following formula (1-a):



(1-a)

in the formula,

R_1 represents a hydrogen atom, a methyl group which may have a substituent, or a group represented by $-CH_2-R_9$, wherein R_9 represents a hydroxyl group or a monovalent organic group,

R_2 represents an alkyl group or a cycloalkyl group.

10. The negative pattern forming method according to any one of claims 1 to 7,

wherein the resin (A) contains a repeating unit having a group capable of decomposing by an action of an acid to produce an alcoholic hydroxyl group as a polar group.

11. The negative pattern forming method according to any one of claims 1 to 10,

wherein a content of an aromatic group-containing repeating unit in the resin (A) is 5 mol% or less based on all repeating units in the resin (A).

12. The negative pattern forming method according to any one of claims 1 to 11,

wherein the resin (A) has a weight average molecular weight of 5,000 or more.

13. The negative pattern forming method according to any one of claims 1 to 12,

wherein the developer containing one or more organic solvents contains at least one kind of an organic solvent selected from the group consisting of a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, an amide-based solvent and an ether-based solvent.

14. The negative pattern forming method according to claim 13,

wherein the one or more organic solvents in the developer is butyl acetate.

15. The negative pattern forming method according to any one of claims 1 to 14,

wherein a water content ratio as the entire developer in the developer containing one or more organic solvents is less than 10 mass%.

16. The negative pattern forming method according to any one of claims 1 to 15,

wherein the developer containing one or more organic solvents contains substantially no water.

17. The negative pattern forming method according to any one of claims 1 to 16, further comprising:

(iv) performing rinsing by using a rinsing solution containing one or more organic solvents.

18. The negative pattern forming method according to any one of claims 1 to 17,

wherein the exposing of the film in the step (ii) is exposure to an ArF excimer laser.

19. The negative pattern forming method according to any one of claims 1 to 18,

wherein the film thickness of the film formed from the chemical amplification resist composition is 600 nm or less.

20. A resist pattern formed by the negative pattern forming method claimed in any one of claims 1 to 19.