Then, it is found that, in such a photomask blank, for example, a phase shift mask blank in which a phase shift film which is a film made of a material containing silicon is formed as a processing film or a reflective mask blank in which an absorption film as a film made of a material containing tantalum is formed, adhesion of a resist film to the film containing chromium is high, and the adhesion of the resist film to the film containing chromium is not deteriorated even in removing the resist film formed on the film containing chromium by using a mixed solution of sulfuric acid and hydrogen peroxide water and forming a resist film again, even in a case where a photomask is manufactured by a general method of manufacturing the photomask, in forming an assist pattern of a line pattern which assists resolution of a main pattern of the photomask, a good resolution limit can be achieved.

In one aspect, the invention provides a photomask blank including: a substrate; a film made of a material containing chromium; and a processing film which is formed to be in contact with a side of the film made of the material containing chromium close to the substrate and is processed by using a pattern of the film made of the material containing chromium as an etching mask,

wherein the film made of the material containing chromium is a stacked film having a three-layer structure including a first layer, a second layer and a third layer from a side apart from the substrate, and each of the first layer, the second layer and the third layer contains chromium, oxygen and nitrogen,

the first layer has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, a nitrogen content of 10 atomic% or less, and a thickness of 20 nm or more,

the second layer has a chromium content of 50 atomic% or more, an oxygen content of 20 atomic% or less, and a nitrogen content of 30 atomic% or more, and

the third layer has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, and a nitrogen content of 10 atomic% or less.

In another aspect, there is provided a photomask blank comprising a substrate, a film made of a chromium-containing material; and a processing film which is formed in contact with that side of the film made of chromium-containing material closer to the substrate, so that it can be processed using a pattern of the film made of the chromium-containing material as an etching mask, wherein the film made of chromium-containing material is a stacked film having a three-layer structure including in order from the side

remote from the substrate, a first layer (311), a second layer (312) and a third layer (313), and each of the first layer, the second layer and the third layer contains chromium, oxygen and nitrogen, the first layer (311) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, a nitrogen content of 10 atomic% or less, and a thickness of 20 nm or more, the second layer (312) has a chromium content of 50 atomic% or more, an oxygen content of 20 atomic% or less, and a nitrogen content of 30 atomic% or more, and the third layer (313) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, and a nitrogen content of 10 atomic% or less.

In a preferred embodiment, the second layer has a thickness of 5 nm or less, and the third layer has a thickness of 5 nm or more.

In a preferred embodiment, the processing film is a film made of a material containing silicon.

In a preferred embodiment, the film made of the material containing chromium is a light shielding film, the film made of the material containing the silicon is a phase shift

film, the photomask blank is a phase shift mask blank, and an optical density of a combination of the light shielding film and the phase shift film is 3 or more with respect to exposure light.

Preferably, the film made of the material containing chromium has a thickness of 40 nm or more and 65 nm or less.

Also preferably, the phase shift film has a phase shift of 175 degrees or more and 185 degrees or less and a transmittance of 6% or more and 30% or less, with respect to the exposure light, and a thickness of 50 nm or more and 90 nm or less.

In a preferred embodiment, the processing film is a film made of a material containing tantalum.

Preferably, the film made of the material containing the tantalum is an absorption film for light in an extreme ultraviolet region, the photomask blank is a reflective mask blank having a reflection film for light in an extreme ultraviolet region, and the reflection film is formed to be in contact with a side of the absorption film close to the substrate.

In a preferred embodiment, the photomask blank further includes a resist film which is in contact with a side of the film made of the material containing chromium apart from the substrate and has a thickness of 50 nm or more and 200 nm or less.

In another aspect, the present disclosure provides a method of manufacturing a photomask from a photomask blank as defined herein comprising patterning the film made of chromium-containing material, and patterning the processing film, using the pattern of the film made of the chromium-containing material as an etching mask.

In yet another aspect, the invention provides a method of manufacturing a photomask having a circuit pattern of the film made of the material containing silicon from the photomask blank according to 3, including steps of:

(A) forming a resist film in contact with a side of the film made of the material containing chromium apart from the substrate;

(C) patterning the resist film to form a resist pattern;

(D) patterning the film made of the material containing chromium by dry etching using a chlorine-based gas containing oxygen by using the resist pattern as an etching mask to form a pattern of the film made of the material containing chromium;

(E) patterning the film made of the material containing silicon by dry etching using a fluorine-based gas by using the pattern of the film made of the material containing

chromium as an etching mask to form a pattern of the film made of the material containing silicon; and

(F) after the step (E), allowing the film made of the material containing chromium to remain in a portion located on an outer peripheral portion of the substrate which is a

region where a circuit pattern of the film made of the material containing the silicon is not formed and removing a pattern of the film made of the material containing chromium other than the outer peripheral portion by dry etching using a chlorine-based gas containing oxygen.

In a preferred embodiment, the method further includes, between the steps (A) and (C), a step of (B) removing the resist film by using a mixed solution of sulfuric acid and hydrogen peroxide water to newly form a resist film to be brought into contact with a side of the film made of the material containing chromium apart from the substrate.

In a still further aspect, the invention provides a photomask having a circuit pattern of a film made of a material containing silicon on a substrate,

wherein a film made of a material containing chromium is formed to be in contact with the film made of the material containing the silicon in a portion located on an outer peripheral portion of the substrate which is a region where a circuit pattern of the film made of the material containing the silicon is not formed,

the film made of the material containing chromium is a stacked film having a three-layer structure including a first layer, a second layer and a third layer from a side apart from the substrate, and each of the first layer, the second layer and the third layer contains chromium, oxygen and nitrogen,

the first layer has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, a nitrogen content of 10 atomic% or less, and a thickness of 20 nm or more,

the second layer has a chromium content of 50 atomic% or more, an oxygen content of 20 atomic% or less, and a nitrogen content of 30 atomic% or more, and

the third layer has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, and a nitrogen content of 10 atomic% or less.

In a further aspect, there is provided a photomask having a circuit pattern of a film made of silicon-containing material on a substrate, wherein a film made of a chromium-containing material is formed to be in contact with said film made of silicon-containing material at an outer peripheral portion of the substrate, being a region where the circuit pattern of the film made of silicon-containing material is not present, the film made of the chromium-containing material is a stacked film having a three-layer structure including, in order from the side remote from the substrate, a first layer, a second layer, and a third layer,

and each of the first layer, the second layer and the third layer contains chromium, oxygen and nitrogen, the first layer has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, a nitrogen content of 10 atomic% or less, and a thickness of 20 nm or more, the second layer has a chromium content of 50 atomic% or more, an oxygen content of 20 atomic% or less, and a nitrogen content of 30 atomic% or more, and the third layer (313) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, and a nitrogen content of 10 atomic% or less.

In a preferred embodiment, the second layer has a thickness of 5 nm or less, and the third layer has a thickness of 5 nm or more.

In a preferred embodiment, the film made of the material containing chromium is a light shielding film, the film made of the material containing the silicon is a phase shift film, the photomask is a phase shift mask, and an optical density of a combination of the light shielding film and the phase shift film is 3 or more, with respect to exposure light.

CLAIMS:

1. A photomask blank comprising: a substrate (1), a film (31) made of a chromium-containing material; and a processing film (21; 23) which is formed in contact with that side of the film (31) made of chromium-containing material closer to the substrate, so that it can be processed using a pattern of the film (31) made of the chromium-containing material as an etching mask,

wherein the film (31) made of chromium-containing material is a stacked film having a three-layer structure including in order from the side remote from the substrate, a first layer (311), a second layer (312) and a third layer (313), and each of the first layer, the second layer and the third layer contains chromium, oxygen and nitrogen,

the first layer (311) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, a nitrogen content of 10 atomic% or less, and a thickness of 20 nm or more,

the second layer (312) has a chromium content of 50 atomic% or more, an oxygen content of 20 atomic% or less, and a nitrogen content of 30 atomic% or more, and

the third layer (313) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, and a nitrogen content of 10 atomic% or less.

2. Photomask blank according to claim 1, wherein the second layer (312) has a thickness of 5 nm or less, and the third layer (313) has a thickness of 5 nm or more.

3. Photomask blank according to claim 1 or 2, wherein the processing film (21) is a film made of a silicon-containing material.

4. The photomask blank according to claim 3, wherein the film (31) made of chromium-containing material is a light shielding film, the film (21) made of silicon-containing material is a phase shift film, the photomask blank is a phase shift mask blank, and the optical density of the combination of the light shielding film (31) and the phase shift film (21) is 3 or more with respect to exposure light.

5. Photomask blank according to claim 4, wherein the film (31) made of the chromium-containing material has a thickness of 40 nm or more and 65 nm or less.

6. Photomask blank according to claim 4 or 5, wherein the phase shift film (21) has a phase shift of 175 degrees or more and 185 degrees or less and a transmittance of 6% or more and 30% or less, with respect to the exposure light, and a thickness of 50 nm or more and 90 nm or less.

7. Photomask blank according to claim 1 or 2, wherein the processing film is a film (23) made of a material containing tantalum.

8. Photomask blank according to claim 7,

wherein the film (23) made of tantalum-containing material is an absorption film for light in an extreme ultraviolet region, the photomask blank is a reflective mask blank having a reflection film (22) for light in an extreme ultraviolet region, and the reflection film is formed in contact with the side of the absorption film (23) closer to the substrate.

9. Photomask blank according to any one of claims 1 to 8, further comprising a resist film (4) which is in contact with the side of the film (31) made of chromium-containing material remote from the substrate and has a thickness of 50 nm or more and 200 nm or less.

10. A method of manufacturing a photomask from a photomask blank as defined in any one of claims 1 to 9, comprising:

patterning the film (31) made of chromium-containing material, and

patterning the processing film (21; 23), using the pattern of the film (31) made of the chromium-containing material as an etching mask.

11. A method of claim 10 for manufacturing a photomask having a circuit pattern of a film made of silicon-containing material, from a photomask blank as defined in any of claims 3 to 6, or as defined in claim 9 when dependent on claim 3, comprising steps of:

(A) forming a resist film (4) in contact with that side of the film (31) made of chromium-containing material remote from the substrate;

(C) patterning the resist film (4) to form a resist pattern (41);

(D) patterning the film (31) made of chromium-containing material by dry etching using a chlorine-based gas containing oxygen, using the resist pattern (41) as an etching mask to form a pattern (31a) of the film made of chromium-containing material;

(E) patterning the film (21) made of silicon-containing material by dry etching using a fluorine-based gas using the pattern (31a) of the film made of chromium-containing material as an etching mask to form a pattern (21a) of the film made of the silicon-containing material; and

(F) after step (E), removing a pattern of the film of chromium-containing material by dry etching using a chlorine-based gas containing oxygen, while allowing a portion (31b) of the film of chromium-containing material to remain at an outer peripheral portion of the substrate, being a region where a circuit pattern of the film (21) made of silicon-containing material is not present.

12. Method according to claim 11, further comprising, between steps (A) and (C), a step (B) of removing the resist film (4) using a mixed solution of sulfuric acid and hydrogen peroxide water to newly form a resist film to be brought into contact with that side of the film made of chromium-containing material remote from the substrate.

13. A photomask having a circuit pattern (21a) of a film (21) made of silicon-containing material on a substrate (1),

wherein a film (31) made of a chromium-containing material is formed to be in contact with said film (21) made of silicon-containing material at an outer peripheral portion of the substrate, being a region where the circuit pattern of the film (21) made of silicon-containing material is not present,

the film (31) made of the chromium-containing material is a stacked film having a three-layer structure including, in order from the side remote from the substrate, a first layer (311), a second layer (312), and a third layer (313), and each of the first layer, the second layer and the third layer contains chromium, oxygen and nitrogen,

the first layer (311) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, a nitrogen content of 10 atomic% or less, and a thickness of 20 nm or more,

the second layer (312) has a chromium content of 50 atomic% or more, an oxygen content of 20 atomic% or less, and a nitrogen content of 30 atomic% or more, and

the third layer (313) has a chromium content of 40 atomic% or less, an oxygen content of 50 atomic% or more, and a nitrogen content of 10 atomic% or less.

14. Photomask according to claim 13, wherein the second layer (312) has a thickness of 5 nm or less, and the third layer has a thickness of 5 nm or more.

15. Photomask according to claim 13 or 14, wherein said film (31) made of chromium-containing material is a light shielding film, said film (21) made of silicon-containing material is a phase shift film, the photomask is a phase shift mask (513), and an optical density of a combination of the light shielding film and the phase shift film is 3 or more, with respect to exposure light.

16. Photomask according to claim 15, wherein the film (31) made of the chromium-containing material has a thickness of 40 nm or more and 65 nm or less.

17. Photomask according to claim 15 or 16, wherein the phase shift film has a phase shift of 175 degrees or more and 185 degrees or less and a transmittance of 6% or more and 30% or less, with respect to exposure light, and a thickness of 50 nm or more and 90 nm or less.

18. Photomask blank according to claim 4 or 6, or photomask according to claim 15 or 17, in which said exposure light is light having a wavelength of 250 nm or less, preferably ArF excimer laser (193 nm) or $F_2$ laser (wavelength 157 nm).