

(including also a state in which a resist layer is formed) before patterning the absorber film is called a reflective mask blank, and is used as a material for the reflective mask.

The reflective mask blank has a basic structure including a low thermal expansion substrate, a multilayer reflection film that is formed thereon and reflects EUV light, and
5 generally, further including an absorber film that is formed on the multilayer reflection film and absorbs EUV light. As the multilayer reflection film, a multilayer reflection film which is ensured a necessary reflectance for EUV light by alternately laminating molybdenum (Mo) films and silicon (Si) films are commonly used. Further, a ruthenium (Ru) film is formed on the multilayer reflection film as a protection film to protect the
10 multilayer reflection film (Patent Document 1: JP-A 2002-122981). On the other hand, tantalum (Ta) which has a relatively large extinction coefficient with respect to EUV light is used for the absorber film (Patent Document 2: JP-A 2002-246299).

Citation List

Patent Document 1: JP-A 2002-122981

15 Patent Document 2: JP-A 2002-246299

SUMMARY

The protection film has function for protecting the multilayer reflection film. However, in addition to function for preventing decrease of reflectance due to repeated
20 EUV exposure to the reflective mask, it is required to have resistance to various dry etchings and cleaning with chemical solutions in a manufacturing process of the reflective mask.

In the manufacturing process of a reflective mask using a reflective mask blank as a material, when an absorber film is dry etched to form a pattern of an absorber film, a
25 certain degree of over-etching is usually performed to control a pattern shape. By performing the over-etching, the protection film is exposed to etching, and is damaged. In particular, for example, when the absorber film is composed of a material containing tantalum (Ta) and nitrogen (N), a gas containing chlorine and being free of oxygen is preferably used as an etching gas. Therefore, the protection film is required to have
30 resistance to dry etching using a gas containing chlorine and being free of oxygen.

Further, when a hard mask pattern which is formed by patterning a hard mask film containing chromium (Cr) is used as an etching mask in forming a pattern to the absorber film, after forming the pattern of the absorber film, usually, the hard mask pattern is

removed by dry etching using a gas containing chlorine and oxygen. The protection film is also exposed to the same dry etching at that time. Therefore, the protection film is also required to have resistance to dry etching using a gas containing chlorine and oxygen.

Furthermore, to remove a resist in manufacturing the reflective mask and to remove
5 contamination in repeated use of the reflective mask, the reflective mask is cleaned with a chemical solution using sulfuric acid-hydrogen peroxide mixture (SPM). Therefore, the protection film is also required to have resistance to SPM cleaning.

If the protection film is damaged, and changes in film quality and thickness are caused in etching in manufacturing the reflective mask or in cleaning in manufacturing or
10 use of the reflective mask, problems such as loss of the function for protecting the multilayer reflection film are occurred in the protection film. A protection film composed of simple ruthenium (Ru) does not have sufficient resistance to dry etching using, particularly, a gas containing chlorine and oxygen. Therefore, the film thickness decreases in removing process of the hard mask pattern, a problem of deterioration in the
15 function for protecting the multilayer reflection film is occurred in the protection film.

So, a protection film added with an additive element such as niobium (Nb) to the protection film containing ruthenium (Ru) has been proposed to enhance the function for protecting the multilayer reflection film by improving the resistance to etching. However, the additive element is a metal which has a lowly standard oxidation-reduction potential
20 compared with ruthenium (Ru), and oxidation reaction on the surface of the protection film tends to proceed by adding the additive element into the protection film. As a result, a rate at which the thickness of the protection film decreases due to SPM cleaning increases, and the damage to the protection film in patterning the absorber film increases by increasing a thickness of a natural oxide layer formed on the surface portion of the
25 protection film after forming the protection film.

As described above, the protection film is variously damaged by over-etching in patterning of the absorber film, removal of the hard mask pattern by etching, removal of the resist and the contamination with using SPM cleaning, and others. Accordingly, the function for protecting the multilayer reflection film in use of the reflective mask is
30 deteriorated when the thickness of the protection film is decreased.

The present disclosure has been made to solve the above problems, and an object of the present disclosure is to provide a reflective mask blank and a reflective mask including

a protection film that has high resistances to dry etching using a gas containing chlorine and being free of oxygen, to dry etching using a gas containing chlorine and oxygen, and to SPM cleaning, and a method for manufacturing the reflective mask.

The inventors have made earnestly studies to solve the above problems. As a
5 result, the inventors found, with respect to a reflective mask blank and a reflective mask that include a protection film for a multilayer reflection film formed on one main surface of a substrate, a protection film that contains ruthenium (Ru) and niobium (Nb), and includes a portion having a low ruthenium (Ru) content in the thickness direction compared with both ruthenium (Ru) contents at the side close to the multilayer reflection film, and the side
10 remotest from the multilayer reflection film. Further, the inventors found that the protection film has high resistances to dry etching using a gas containing chlorine and being free of oxygen, to dry etching using a gas containing chlorine and oxygen, and to SPM cleaning.

In one aspect, the disclosure provides a reflective mask blank (101, 102, 103, 104,
15 105, 106) including a substrate (1), a multilayer reflection film (2) that is formed on one main surface of the substrate and reflects exposure light, and a protection film (3) that is formed on the multilayer reflection film wherein

the protection film (3) contains ruthenium (Ru) and niobium (Nb),

the protection film (3) includes a portion having a low ruthenium (Ru) content in
20 the thickness direction compared with both ruthenium (Ru) contents at the side close to the multilayer reflection film and at the side remotest from the multilayer reflection film,

characterized in that: the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not less than 50 at%.

Preferably, the portion having a low ruthenium (Ru) content in the protection film
25 contains niobium (Nb), and the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not more than 85 at%.

Preferably, the ruthenium (Ru) content of the protection film at the side close to the multilayer reflection film is not less than 95 at%, and

the ruthenium (Ru) content of the protection film at the side remotest from the
30 multilayer reflection film is not less than 90 at%.

Preferably, the reflective mask blank includes an absorber film that is formed on the protection film and absorbs the exposure light wherein

the absorber film contains tantalum (Ta) and nitrogen (N).

Preferably, the reflective mask blank further includes a hard mask film that contains chromium (Cr) on the absorber film.

Preferably, the protection film consists of a first layer, a second layer and a third layer in this order from the multilayer reflection film side,

5 the first layer contains ruthenium (Ru) and does not contain substantively any other elements except for ruthenium (Ru),

 the second layer contains niobium (Nb), and

 the third layer contains ruthenium (Ru) and does not contain substantively any other elements except for ruthenium (Ru).

10 Preferably, the second layer further contains ruthenium (Ru).

 Preferably, the protection film has an average ruthenium (Ru) content in the whole of the protection film of not less than 50 at% and not more than 95 at%.

 Preferably, the reflective mask blank includes an absorber film that is formed on the protection film and absorbs the exposure light wherein

15 the absorber film contains tantalum (Ta) and nitrogen (N).

 Preferably, the reflective mask blank includes a hard mask film that contains chromium (Cr) on the absorber film.

 In another aspect, the disclosure provides a reflective mask (103a, 104a, 105a, 106a) including a substrate (1), a multilayer reflection film (2) that is formed on one main surface
20 of the substrate and reflects exposure light, a protection film (3) that is formed on the multilayer reflection film, and a pattern (4a) of an absorber film (4) that is formed on the protection film and absorbs the exposure light wherein

 the protection film (3) contains ruthenium (Ru) and niobium (Nb),

 the protection film (3) includes a portion having a low ruthenium (Ru) content in
25 the thickness direction compared with both ruthenium (Ru) contents at the side close to the multilayer reflection film and at the side remotest from the multilayer reflection film,

 characterized in that: the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not less than 50 at%.

 Preferably, the portion having a low ruthenium (Ru) content in the protection film
30 contains niobium (Nb), and the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not more than 85 at%.

Preferably, the ruthenium (Ru) content of the protection film at the side close to the multilayer reflection film is not less than 95 at%, and

the ruthenium (Ru) content of the protection film at the side remotest from the multilayer reflection film is not less than 90 at%,

Preferably, the protection film consists of a first layer, a second layer and a third layer in this order from the multilayer reflection film side,

5 the first layer contains ruthenium (Ru) and does not contain substantively any other elements except for ruthenium (Ru),

 the second layer contains niobium (Nb), and

 the third layer contains ruthenium (Ru) and does not contain substantively any other elements except for ruthenium (Ru).

10 Preferably, the second layer further contains ruthenium (Ru).

 Preferably, the protection film has an average ruthenium (Ru) content in the whole of the protection film of not less than 50 at% and not more than 95 at%.

 In another aspect, the disclosure provides a method for manufacturing a reflective mask (103a, 104a, 105a, 106a) including the steps of

15 forming a pattern of a resist film on the absorber film (4) of the reflective mask blank,

 forming a pattern (4a) of the absorber film by dry etching using a gas containing chlorine and being free of oxygen with using the pattern of the resist film as an etching mask,

20 after the step of forming the pattern of the absorber film, removing the pattern of the resist film by SPM cleaning.

 In another aspect, the disclosure provides a method for manufacturing a reflective mask (103a, 104a, 105a, 106a) including the steps of

25 forming a pattern of a resist film on the hard mask film (5) of the reflective mask blank,

 forming a pattern (5a) of the hard mask film by dry etching using a gas containing chlorine and oxygen with using the pattern of the resist film as an etching mask,

30 forming a pattern (4a) of the absorber film (4) by dry etching using a gas containing chlorine and being free of oxygen with using the pattern of the hard mask film as an etching mask,

 after the step of forming the pattern of the absorber film, removing the pattern of the resist film by SPM cleaning,

CLAIMS:

1. A reflective mask blank (101, 102, 103, 104, 105, 106) comprising a substrate (1), a multilayer reflection film (2) that is formed on one main surface of the substrate and
5 reflects exposure light, and a protection film (3) that is formed on the multilayer reflection film wherein
the protection film (3) comprises ruthenium (Ru) and niobium (Nb),
the protection film (3) comprises a portion having a low ruthenium (Ru) content in the thickness direction compared with both ruthenium (Ru) contents at the side close to the
10 multilayer reflection film and at the side remotest from the multilayer reflection film,
characterized in that: the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not less than 50 at%.
2. The reflective mask blank of claim 1 wherein
15 the portion having a low ruthenium (Ru) content in the protection film comprises niobium (Nb), and the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not more than 85 at%.
3. The reflective mask blank of claim 1 or 2 wherein
20 the ruthenium (Ru) content of the protection film at the side close to the multilayer reflection film is not less than 95 at%, and
the ruthenium (Ru) content of the protection film at the side remotest from the multilayer reflection film is not less than 90 at%.
- 25 4. The reflective mask blank of any one of claims 1 to 3 wherein
the protection film (3) consists of a first layer (31), a second layer (32) and a third layer (33) in this order from the multilayer reflection film side,
the first layer (31) comprises ruthenium (Ru) and does not comprise substantively any other elements except for ruthenium (Ru),
30 the second layer (32) comprises niobium (Nb) and ruthenium (Ru), and
the third layer (33) comprises ruthenium (Ru) and does not comprise substantively any other elements except for ruthenium (Ru).

5. The reflective mask blank of any one of claims 1 to 4 wherein the protection film (3) has an average ruthenium (Ru) content in the whole of the protection film of not less than 50 at% and not more than 95 at%.
- 5 6. The reflective mask blank of any one of claims 1 to 5 comprising an absorber film (4) that is formed on the protection film and absorbs the exposure light wherein the absorber film (4) comprises tantalum (Ta) and nitrogen (N).
- 10 7. The reflective mask blank of claim 6 further comprising a hard mask film (5) that comprises chromium (Cr) on the absorber film (4).
8. A reflective mask (103a, 104a, 105a, 106a) comprising a substrate (1), a multilayer reflection film (2) that is formed on one main surface of the substrate and reflects exposure light, a protection film (3) that is formed on the multilayer reflection film, and a pattern (4a) of an absorber film (4) that is formed on the protection film and absorbs the exposure light wherein
- 15 the protection film (3) comprises ruthenium (Ru) and niobium (Nb),
the protection film (3) comprises a portion having a low ruthenium (Ru) content in the thickness direction compared with both ruthenium (Ru) contents at the side close to the multilayer reflection film and at the side remotest from the multilayer reflection film,
- 20 characterized in that: the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not less than 50 at%.
- 25 9. The reflective mask of claim 8 wherein the portion having a low ruthenium (Ru) content in the protection film comprises niobium (Nb), and the portion having a low ruthenium (Ru) content in the protection film has a ruthenium (Ru) content of not more than 85 at%.
- 30 10. The reflective mask of claim 8 or 9 wherein the ruthenium (Ru) content of the protection film at the side close to the multilayer reflection film is not less than 95 at%, and

the ruthenium (Ru) content of the protection film at the side remotest from the multilayer reflection film is not less than 90 at%,

11. The reflective mask of any one of claims 8 to 10 wherein
5 the protection film (3) consists of a first layer (31), a second layer (32) and a third layer (33) in this order from the multilayer reflection film side,
the first layer (31) comprises ruthenium (Ru) and does not comprise substantively any other elements except for ruthenium (Ru),
the second layer (32) comprises niobium (Nb) and ruthenium (Ru), and
10 the third layer (33) comprises ruthenium (Ru) and does not comprise substantively any other elements except for ruthenium (Ru).

12. The reflective mask of any one of claims 8 to 11 wherein the protection film (3) has an average ruthenium (Ru) content in the whole of the protection film of not less than 50
15 at% and not more than 95 at%.

13. A method for manufacturing a reflective mask (103a, 104a, 105a, 106a) comprising the steps of
forming a pattern of a resist film on the absorber film (4) of the reflective mask
20 blank of claim 6,
forming a pattern (4a) of the absorber film by dry etching using a gas containing chlorine and being free of oxygen with using the pattern of the resist film as an etching mask,
after the step of forming the pattern of the absorber film, removing the pattern of
25 the resist film by SPM cleaning.

14. A method for manufacturing a reflective mask (103a, 104a, 105a, 106a) comprising the steps of
forming a pattern of a resist film on the hard mask film (5) of the reflective mask
30 blank of claim 7,
forming a pattern (5a) of the hard mask film by dry etching using a gas containing chlorine and oxygen with using the pattern of the resist film as an etching mask,

forming a pattern (4a) of the absorber film (4) by dry etching using a gas containing chlorine and being free of oxygen with using the pattern of the hard mask film as an etching mask,

- 5 after the step of forming the pattern of the absorber film, removing the pattern of the resist film by SPM cleaning,

after the step of removing the pattern of the resist film, removing the pattern of the hard mask film by dry etching using a gas containing chlorine and oxygen.