necessary etching resistance and high reflectance, and is hard to be decreased reflectance when the multilayer reflection film is heated.

In one aspect, the present disclosure provides a substrate with a multilayer reflection film for an EUV mask blank comprising a substrate, and a multilayer reflection film formed on the substrate, wherein the multilayer reflection film comprises a Si/Mo laminated portion in which Si layers and Mo layers are alternately laminated, and a protection layer containing Ru formed on the Si/Mo laminated portion and in contact with the Si/Mo laminated portion, as the uppermost layer, the protection layer comprises a lower layer formed in contact with the Si/Mo laminated portion, and an upper layer formed at the side remotest from the substrate, the lower layer is composed of Ru, and the upper layer is composed of a material containing Ru and at least one selected from the group consisting of metals other than Ru, and metalloids, and the upper layer has a graded composition in which a content of the metal or metalloid continuously increases to the side remote from the substrate in the thickness direction of the upper layer, or the upper layer consists of two or more of sublayers and has a graded composition in which contents of the metal or metalloid of the sublayers increase in stepwise to the side remote from the substrate in the thickness direction of the upper layer.

Further, the inventors have been found that in forming the multilayer reflection film of a substrate with a multilayer reflection film for an EUV mask blank and a EUV mask blank, it is very important for achieving high reflectance that, after forming the Si/Mo laminated portion, the Mo/Si laminated portion is provided to formation of the protection film without contacting to gases reactable to the Mo/Si laminated portion.

In one aspect, the invention provides a substrate with a multilayer reflection film for an EUV mask blank including a substrate, and a multilayer reflection film formed on the substrate, wherein

the multilayer reflection film includes a Si/Mo laminated portion in which Si layers and Mo layers are alternately laminated, and a protection layer containing Ru formed on the Si/Mo laminated portion and in contact with the Si/Mo laminated portion, as the uppermost layer,

the protection layer includes a lower layer formed in contact with the Si/Mo laminated portion, and an upper layer formed at the side remotest from the substrate,

the lower layer is composed of Ru, and

the upper layer is composed of a material containing Ru and at least one selected from the group consisting of metals other than Ru, and metalloids.

Preferably, the metals other than Ru are transition metals having a low standard oxidation-reduction potential compared with that of Ru.

Preferably, the upper layer is composed of a material containing Ru and at least one selected from the group consisting of Nb, Zr, Ti, Cr and Si.

Preferably, the upper layer is composed of a material containing Ru and at least one selected from the group consisting of metals and metalloids that have a low etching rate compared with that of Ru in a dry etching using an etching gas containing O_2 gas and Cl_2 gas.

Preferably, the upper layer has a graded composition in which a content of the metal or metalloid continuously increases to the side remote from the substrate in the thickness direction of the upper layer, or the upper layer consists of two or more of sublayers and has a graded composition in which contents of the metal or metalloid of the

CLAIMS:

1. A substrate with a multilayer reflection film for an EUV mask blank comprising a substrate, and a multilayer reflection film formed on the substrate, wherein

the multilayer reflection film comprises a Si/Mo laminated portion in which Si layers and Mo layers are alternately laminated, and a protection layer containing Ru formed on the Si/Mo laminated portion and in contact with the Si/Mo laminated portion, as the uppermost layer,

the protection layer comprises a lower layer formed in contact with the Si/Mo laminated portion, and an upper layer formed at the side remotest from the substrate,

the lower layer is composed of Ru, and

the upper layer is composed of a material containing Ru and at least one selected from the group consisting of metals other than Ru, and metalloids, and

the upper layer has a graded composition in which a content of the metal or metalloid continuously increases to the side remote from the substrate in the thickness direction of the upper layer, or the upper layer consists of two or more of sublayers and has a graded composition in which contents of the metal or metalloid of the sublayers increase in stepwise to the side remote from the substrate in the thickness direction of the upper layer.

2. The substrate of claim 1, wherein the metals other than Ru are transition metals having a low standard oxidation-reduction potential compared with that of Ru.

3. The substrate of claim 1 or 2, wherein the upper layer is composed of a material containing Ru and at least one selected from the group consisting of Nb, Zr, Ti, Cr and Si.

4. The substrate of any one of claims 1 to 3, wherein the upper layer is composed of a material containing Ru and at least one selected from the group consisting of metals and metalloids that have a low etching rate compared with that of Ru in a dry etching using an etching gas containing O_2 gas and Cl_2 gas.

5. The substrate of any one of claims 1 to 4, wherein the upper layer further contains oxygen.

6. The substrate of any one of claims 1 to 5, wherein a layer containing Si and N intervenes at one or more portions between the Si layer and the Mo layer of the Si/Mo laminated portion, and is contact with both of the Si layer and the Mo layer.

7. The substrate of claim 6, wherein the layer containing Si and N has a thickness of not more than 2 nm.

8. The substrate of any one of claims 1 to 7, wherein the protection layer is contact with the Mo layer of the Si/Mo laminated portion.

9. The substrate of claim 6, wherein the uppermost part of the multilayer reflection film consists of, from the side remote from the substrate, the protection layer, the Mo layer, a layer containing Si and N, and the Si layer.

10. The substrate of claim 9, wherein in the uppermost part, the protection layer has a thickness of not more than 4 nm, the Mo layer has a thickness of not more than 1 nm, the layer containing Si and N has a thickness of not more than 2 nm, and the Si layer has a thickness of not more than 4 nm.

11. The substrate of any one of claims 1 to 10, wherein the Si/Mo laminated portion comprises not less than 30 of three-layer laminated structure units, and the three-layer laminated structure unit consists of, from the substrate side,

i) the Si layer, a layer containing Si and N formed in contact with the Si layer, and the Mo layer formed in contact with the layer containing Si and N, or;

ii) the Mo layer, a layer containing Si and N formed in contact with the Mo layer, and the Si layer formed in contact with the layer containing Si and N.

12. The substrate of any one of claims 1 to 10, wherein the Si/Mo laminated portion comprises not less than 30 of four-layer laminated structure units, and the four-layer

laminated structure unit consists of, from the substrate side, the Si layer, a layer containing Si and N formed in contact with the Si layer, the Mo layer formed in contact with the layer containing Si and N, and a layer containing Si and N formed in contact with the Mo layer.

13. The substrate of any one of claims 1 to 12, wherein the multilayer reflection film has a peak reflectance of not less than 65% with respect to EUV light of the wavelength range of 13.4 to 13.6 nm at an incident angle of 6°.

14. A manufacturing method for the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 1 to 13, the method comprising the step of

(A) forming the Si/Mo laminated portion by sputtering, wherein

the sputtering is performed by a magnetron sputtering apparatus comprising a chamber, wherein in the chamber,

one or more Mo targets and one or more Si targets are attachable;

powers are individually appliable to the Mo target and the Si target;

the substrate and each of the targets are disposed in offset arrangement;

none of shield members are disposed between the substrate and each of the targets;

the substrate is rotatable along its main surface; and

nitrogen-containing gas is introducible.

15. A manufacturing method for the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 1 to 13, the method comprising the step of

(B) forming the protection layer by sputtering, wherein

the sputtering is performed by a magnetron sputtering apparatus comprising a chamber, wherein in the chamber,

one or more Ru targets and one or more targets containing at least one selected from the group consisting of metals other than Ru, and metalloids are attachable;

powers are individually appliable to the Ru target and the target containing at least one selected from the group consisting of metals other than Ru, and metalloids;

the substrate and each of the targets are disposed in offset arrangement;

none of shield members are disposed between the substrate and each of the targets;

the substrate is rotatable along its main surface; and

oxygen-containing gas is introducible.

16. An EUV mask blank comprising the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 1 to 13, and an absorber film containing Ta or Cr formed on the multilayer reflection film.

17. An EUV mask blank comprising the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 1 to 13, an absorber film containing Ta and being free of Cr formed on the multilayer reflection film, and a hard mask film which contains Cr and acts as an etching mask in dry etching for the absorber film.