

TITLE OF THE INVENTION

Substrate with Multilayer Reflection Film for EUV Mask Blank,
Manufacturing Method Thereof, and EUV Mask Blank

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TECHNICAL FIELD

The present invention relates to an EUV mask blank which is a material for
15 manufacturing an EUV mask used for manufacturing semiconductor devices such as LSIs,
a substrate with a multilayer reflection film for an EUV mask blank used for manufacturing
an EUV mask blank, and a manufacturing method thereof.

BACKGROUND ART

20 In a manufacturing process of semiconductor devices, a photolithography technique
in which a circuit pattern formed on a transfer mask is transferred onto a semiconductor
substrate (semiconductor wafer) through a reduction projection optical system with
irradiating exposure light to the transfer mask is repeatedly used. Conventionally, a
mainstream wavelength of the exposure light is 193 nm by argon fluoride (ArF) excimer
25 laser light. A pattern with dimensions smaller than exposure wavelength has finally been
formed by adopting a process called multi-patterning in which exposure processes and
processing processes are combined multiple times.

However, since it is necessary to form a further fine pattern under continuous
miniaturization of device patterns, EUV lithography technique using, as exposure light,
30 EUV (extreme ultraviolet) light having a wavelength shorter than ArF excimer laser light
was developed. EUV light is light having a wavelength of, for example, about 10 to 20
nm, more specifically, light having a wavelength of around 13.5 nm. This EUV light has

a very low transmission to a substance and cannot be utilized for a conventional transmissive projection optical system or a mask, thus, reflection type optical elemental devices are applied. Therefore, a reflective mask is also proposed as a mask for the pattern transfer. The reflective mask includes a multilayer reflection film that is formed on a substrate and reflects EUV light, and a patterned absorber film that is formed on the multilayer reflection film and absorbs EUV light. Meanwhile, a material (also including a material in which a resist layer is formed) before patterning the absorber film is called a reflective mask blank, and this is used as a material for the reflective mask. Generally, a reflective mask and a reflective mask blank that reflect EUV light are referred to as an EUV mask and an EUV mask blank, respectively.

The EUV 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 an absorber film that is formed thereon and absorbs EUV light. As the multilayer reflection film, a Mo/Si multilayer reflection film which is obtained a necessary reflectance for EUV light by alternately laminating molybdenum (Mo) films and silicon (Si) films is usually used. Further, as a protection film for protecting the multilayer reflection film, a ruthenium (Ru) film or a film composed of a mixture of Ru and niobium (Nb) and/or zirconium (Zr) is formed as the outermost layer of the multilayer reflection film. On the other hand, as the absorber film, a material containing tantalum (Ta) or chromium (Cr) as a main component, which has a relatively large extinction coefficient with respect to EUV light, is used.

Citation List

Patent Document 1: JP-A 2005-516282

Patent Document 2: WO 2015/012151 A1

SUMMARY OF THE INVENTION

It is required that the multilayer reflection film has a high reflectance to EUV light. However, in the portion in which the Mo layer and the Si layer are alternately laminated, an interdiffusion layer in which both components Si and Mo are mixed is formed between the Mo layer and the Si layer. In this case, only a low reflectance which deviates from the theoretical reflectance in the laminated the Mo layers and the Si layers is obtained. Further, when the multilayer reflection film is heated during mask processing or exposure

with EUV light using the mask, the interdiffusion layer becomes thicker or changes its nature, resulting further decrease of reflectance.

The present invention has been made to solve the above problems, and an object of the present invention is to provide a substrate with a multilayer reflection film for an EUV mask blank including the multilayer reflection film that has high reflectance, and is hard to be decreased reflectance when the multilayer reflection film is heated, a manufacturing method of the substrate, and an EUV mask blank including the substrate.

The inventors have been found that in a multilayer reflection film used for an EUV mask blank which is constructed by a Si/Mo laminated portion in which Si layers and Mo layers are alternately laminated, when 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, preferably, when the multilayer reflection film is constructed by such a Si/Mo laminated portion and a protection layer containing Ru formed in contact with the Si/Mo laminated portion, as the uppermost layer of the multilayer reflection film, a substrate with a multilayer reflection film for an EUV mask blank, and an EUV mask blank have high reflectance, and is hard to be decreased reflectance when the multilayer reflection film is heated.

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 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.

Preferably, the layer containing Si and N has a thickness of not more than 2 nm.

Preferably, the multilayer reflection film further includes a protection layer containing Ru formed in contact with the Si/Mo laminated portion, as the uppermost layer.

Preferably, the protection layer is contact with the Mo layer of the Si/Mo laminated portion.

Preferably, 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.

5 Preferably, 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.

10 Preferably, the Si/Mo laminated portion includes 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.

15 Preferably, the Si/Mo laminated portion includes 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.

20 Preferably, 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°.

25 In another aspect, the invention provides a manufacturing method for the substrate with a multilayer reflection film for an EUV mask blank, the method including the step of (A) forming the Si/Mo laminated portion by sputtering, wherein the sputtering is performed by a magnetron sputtering apparatus including a chamber, wherein in the chamber,

30 one or more Mo targets and one or more Si targets are attachable;
powers are individually applicable 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.

In another aspect, the invention provides a manufacturing method for the substrate with a multilayer reflection film for an EUV mask blank, the method including the steps of

- 5 (A) forming the Si/Mo laminated portion by sputtering, and
(B) forming the protection layer by sputtering, wherein

after the step (A), the Mo/Si laminated portion is provided to the step (B) without contacting to gases reactable to the Mo/Si laminated portion that has been formed in the step (A).

- 10 Preferably, the step (A) is performed in one sputter chamber, the substrate on which the Mo/Si laminated portion has been formed is transferred to the other sputter chamber, and then, the step (B) is performed in the other sputter chamber.

- Preferably, a transfer chamber is provided between the one and other sputter chambers, the transfer chamber is capable of communicating with each of the sputter
15 chambers individually or with both of the sputter chambers at the same time, and the substrate on which the Mo/Si laminated portion has been formed is transferred from the one sputter chamber via the transfer chamber to the other sputter chamber.

- Preferably, the substrate is transferred under vacuum both in the transfer from the one sputter chamber to the transfer chamber, and the transfer from the transfer chamber to
20 the other sputter chamber.

Preferably, the Si/Mo laminated portion includes 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
25 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.

- Preferably, the Si/Mo laminated portion includes not less than 30 of four-layer laminated structure units, and the four-layer laminated structure unit consists of, from the
30 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.

Preferably, 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°.

5 In another aspect, the invention provides an EUV mask blank including the substrate with a multilayer reflection film for an EUV mask blank, and an absorber film containing Ta or Cr formed on the multilayer reflection film.

In the other aspect, the invention provides an EUV mask blank including the substrate with a multilayer reflection film for an EUV mask blank, an absorber film containing Ta and being free of Cr formed on the multilayer reflection film, and a hard
10 mask film which contains Cr and acts as an etching mask in dry etching for the absorber film.

ADVANTAGEOUS EFFECTS OF THE INVENTION

According to the invention, a substrate with a multilayer reflection film for an EUV
15 mask blank including the multilayer reflection film that has high reflectance, and is hard to be decreased reflectance when the multilayer reflection film is heated, and an EUV mask blank including the substrate can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

20 FIG. 1 is an intermediate omitted partial cross-sectional view of an example of a substrate with a multilayer reflection film for an EUV mask blank of the invention.

FIG. 2 is an intermediate omitted partial cross-sectional view for explaining a substrate with a multilayer reflection film for an EUV mask blank including an ideal multilayer reflection film consisting of a Si/Mo laminated portion and a protection layer.

25 FIG. 3 is an intermediate omitted partial cross-sectional view for explaining a reflective mask blank including a conventional multilayer reflection film consisting of a Si/Mo laminated portion and a protection layer.

FIG. 4 is a conceptual diagram showing an example of a sputtering apparatus suitable for forming a multilayer reflection film of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A substrate with a multilayer reflection film for an EUV mask blank of the invention includes a substrate, and a multilayer reflection film formed on the substrate (on one main surface or the front surface of the substrate) and reflects exposure light, in particular, a multilayer reflection film that reflects EUV light. The multilayer reflection film may be formed in contact with the one main surface of the substrate. Further, an undercoat film may be formed between the substrate and the multilayer reflection film. A wavelength of EUV light used for EUV lithography using EUV light as exposure light is 13 to 14 nm, and is usually light having a wavelength of about 13.5 nm (for example, 13.4 to 13.6 nm).

FIG. 1 is an intermediate omitted partial cross-sectional view of an example of a substrate with a multilayer reflection film for an EUV mask blank of the invention. The substrate with a multilayer reflection film for an EUV mask blank 10 includes a multilayer reflection film 2 formed on one main surface and in contact with the one main surface of the substrate 1.

The substrate preferably has low thermal expansion property, and, for example, the substrate is preferably composed of a material having a coefficient of thermal expansion within $\pm 2 \times 10^{-8}/\text{C}^\circ$, preferably $\pm 5 \times 10^{-9}/\text{C}^\circ$. Further, a substrate which is sufficiently flattened is preferably used, a surface roughness RMS of the main surface of the substrate is preferably not more than 0.5 nm, more preferably not more than 0.2 nm. Such a surface roughness can be obtained by polishing the substrate.

The multilayer reflection film in an EUV mask is a film that reflects EUV light as exposure light. In the invention, the multilayer reflection film includes a Si/Mo laminated portion consisting of multiple layers in which Si (silicon) layers and Mo (molybdenum) layers are alternately laminated. In the Si / Mo laminated portion, a Si layer composed of a material having a relatively high refractive index with respect to EUV light, and a Mo layer composed of a material having a relatively low refractive index with respect to EUV light are periodically laminated. The Si layer and the Mo layer are layers formed of a simple substance of silicon and a simple substance of molybdenum, respectively. The number of laminated layers of the Si layer and the Mo layer is preferably, for example, not less than 40 cycles (not less than 40 layers, respectively), and preferably not more than 60 cycles (not more than 60 layers, respectively). A thickness of the Si layer and the Mo

layer of the Si/Mo laminated portion is appropriately set according to the exposure wavelength. The thickness of the Si layer is preferably not more than 5 nm, and the thickness of the Mo layer is not more than 4 nm. A lower limit of the thickness of the Si layer is normally not less than 1 nm, however, not limited thereto. A lower limit of the thickness of the Mo layer is normally not less than 1 nm, however, not limited thereto. The thickness of the Si layer and the Mo layer may be set so as to obtain a high reflectance for EUV light. Further, the thickness of each of the Si layers and each of the Mo layers may be constant or different in each layer. A total thickness of the Si/Mo laminated portion is normally about 250 to 450 nm.

In the invention, 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. The layer containing Si and N is preferably free of oxygen. As the layer containing Si and N, in particular, SiN layer is preferable. Here, "SiN" means that the constituent elements are only Si and N. A nitrogen content of the layer containing Si and N is preferably not less than 1 at%, more preferably not less than 5 at%, and not more than 60 at%, more preferably not more than 57 at%. The layer containing Si and N has a thickness of preferably not more than 2 nm, more preferably not more than 1 nm. A lower limit of the thickness of the layer containing Si and N is preferably not less than 0.1 nm, however not limited thereto.

The layer containing Si and N is formed at one or more portions between the Si layer and the Mo layer constituting the Si/Mo laminated portion. The layer containing Si and N may be formed at a part or all of the substrate side (lower side) of the Mo layer, and a part or all of the side remote from the substrate (upper side) of the Mo layer. The layer containing Si and N is more preferably formed at all portions between the Si layer and the Mo layer.

Particularly, in the viewpoint of obtaining high reflectance, the Si/Mo laminated portion preferably includes not less than 30, more preferably not less than 40 of three-layer laminated structure units. The three-layer laminated structure unit consist of, from the substrate side; i) the Si layer, the 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, the 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. Further, the Si/Mo laminated

portion preferably includes not less than 30, more preferably not less than 40 of four-layer laminated structure units. The four-layer laminated structure unit consists of, from the substrate side, the Si layer, the 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
5 containing Si and N formed in contact with the Mo layer. Upper limits of the three-layer laminated structure unit and the four-layer laminated structure units are not more than 60, respectively.

In the invention, the Si/Mo laminated portion shown in FIG. 1 is exemplified as a concrete example. In the multilayer reflection film 2 of the substrate with a multilayer
10 reflection film for an EUV mask blank 10 shown in FIG. 1, the Si/Mo laminated portion 21 is formed in contact with the substrate 1. In the Si/Mo laminated portion 21, the Si layers 211 and the Mo layers 212 are alternately laminated. In this case, the Si layer 211 is disposed at the side closest to the substrate 1, and the Mo layer 212 is disposed at the side remotest from the substrate 1. Further, the layer containing Si and N 213 is formed at
15 each of the portions between the Si layer 211 and the Mo layer 212, and the layer containing Si and N 213 is contact with the Si layer 211 and the Mo layer 212. Thus, in this case, the Si/Mo laminated portion 21 includes the three-layer laminated structure unit consist of, from the substrate side, the Si layer 211, the layer containing Si and N 213, and the Mo layer 212, and the three-layer laminated structure unit consist of, from the substrate
20 side, the Mo layer 212, the layer containing Si and N 213, and the Si layer 211. Further, the Si/Mo laminated portion 21 includes the four-layer laminated structure unit consist of, from the substrate side, the Si layer 211, the layer containing Si and N 213, the Mo layer 212, and the layer containing Si and N 213.

The Si/Mo laminated portion is formed by alternately laminating the Si layers and
25 the Mo layers. FIG. 2 is an intermediate omitted partial cross-sectional view for explaining a substrate with a multilayer reflection film for an EUV mask blank including an ideal multilayer reflection film consisting of a Si/Mo laminated portion and a protection layer. FIG. 3 is an intermediate omitted partial cross-sectional view for explaining a reflective mask blank including a conventional multilayer reflection film consisting of a
30 Si/Mo laminated portion and a protection layer. In case that the Si/Mo laminated portion 21 of the multilayer reflection film 2 of the substrate with a multilayer reflection film for an EUV mask blank 10 is formed by laminating directly on the Si layers and the Mo layers

each other, the state of the Si/Mo laminated portion 21 consisting of only the Si layers 211 and the Mo layers 212 in which the Si layers and the Mo layers are contacted each other is ideal, as shown in FIG. 2. In such a Si/Mo laminated portion 21, a theoretical reflectance can be obtained by the Si/Mo laminated portion consisting of only the Si layers and the Mo
5 layers.

It is not impossible in principle to form the Si/Mo laminated portion having this structure. However, when the Si/Mo laminated portion is formed by a realistic method, in reality, as shown in FIG. 3, Si and Mo are mixed at the portion where the Si layer 211 and the Mo layer 212 are contacted each other, and as a result, an interdiffusion layer 21a
10 consisting of Si and Mo is unintentionally formed at this portion. When such an interdiffusion layer consisting of Si and Mo is formed, a reflectance of the Si/Mo laminated portion is decreased from the theoretical reflectance obtained by the Si/Mo laminated portion consisting of only the Si layers and the Mo layers. Further, when the multilayer reflection film is heated in mask processing or in exposure by EUV light using a mask, the
15 interdiffusion layer consisting of Si and Mo becomes thicker, or the interdiffusion layer consisting of Si and Mo changes in its nature, resulting in further decrease of reflectance.

On the other hand, when the layer containing Si and N is formed between the Si layer and the Mo layer and in contact with both of the Si layer and the Mo layer, formation of the interdiffusion layer consisting of Si and Mo that causes reduction of reflectance is
20 suppressed. Therefore, reduction of reflectance from the theoretical reflectance obtained by the Si/Mo laminated portion consisting of only the Si layers and the Mo layers is suppressed, and a high reflectance is accomplished in compared with a conventional reflectance. In addition, the portion between the Si layer and the Mo layer where the layer containing Si and N is not formed, the above-mentioned interdiffusion layer
25 consisting of Si and Mo is normally formed in contact with both of the Si layer and the Mo layer. However, in the Si/Mo laminated portion of the multilayer reflection film of the invention, formation of the interdiffusion layer consisting of Si and Mo is suppressed at the portion between the Si layer and Mo layer where the layer containing Si and N is formed. Therefore, reduction of reflectance caused by heat is suppressed in compared with the
30 conventional multilayer reflection film in which the interdiffusion layer consisting of Si and Mo is formed at all of the portions between the Si layer and the Mo layer. From this point of view, the layer containing Si and N may be formed a part of the portions between the Si

layer and Mo layer. However, it is advantageous that the layers containing Si and N are formed at many of the portions between the Si layer and the Mo layer, and it is particularly advantageous that the layers containing Si and N are formed at all of the portions between the Si layer and the Mo layer.

5 In the invention, the multilayer reflection film preferably includes a protection layer formed in contact with the Si/Mo laminated portion, as the uppermost layer. When the uppermost layer is the Si layer or the Mo layer, the layer is etched by dry etching using a fluorine-containing gas. Therefore, it is effective that the protection layer is formed on the Si/Mo laminated portion. The protection layer is also called a capping layer, and acts
10 as an etching stopper when forming an absorber pattern from an absorber film formed on the protection layer. Therefore, a material having different etching properties from that of the absorber film is used for the protection layer. The protection layer is preferably effective also for protecting the multilayer reflection film when correcting the absorber pattern.

15 In the invention, the protection layer shown in FIG. 1 is exemplified as a concrete example. In the multilayer reflection film 2 of the substrate with a multilayer reflection film for an EUV mask blank 10, the protection layer 22 is formed in contact with the Si/Mo laminated portion 21.

As a material for the protection layer, a material containing ruthenium (Ru) is used.
20 As the material containing Ru, simple substance Ru, or a Ru compound in which niobium (Nb) and/or zirconium (Zr) are added is preferably used. A thickness of the protection layer is normally not more than 5 nm, in particular, preferably not more than 4 nm. A lower limit of the thickness of the protection layer is normally not less than 2 nm.

In the Si/Mo laminated portion, the layer disposed at the side closest to the
25 substrate may be the Si layer or the Mo layer. On the other hand, the layer disposed at the side remotest from the substrate may be the Si layer or the Mo layer, however, the Mo layer is preferable. The layer contacted to the protection layer in the Si/Mo laminated portion is preferably the Mo layer.

In case that the layer contacted to the protection layer in the Si/Mo laminated
30 portion is the Si layer, when the protection layer composed of a material containing Ru is directly contacted to the Si/Mo laminated portion, a state in which the Si layer 211 of the Si/Mo laminated portion 21 and the protection layer 22 are contacted each other, as shown

in FIG. 2, is ideal. In such a state, decrease of reflectance in the multilayer reflection film 2 due to the protection layer 22 is limited, and a high reflectance can be obtained.

It is not impossible in principle to form the state. However, when the protection layer is formed by a realistic method, in reality, as shown in FIG. 3, Si and Ru are mixed at the portion where the Si layer 211 and the protection layer 22 are contacted each other, and as a result, an interdiffusion layer 21b consisting of Si and Ru is unintentionally formed at this portion. When such an interdiffusion layer consisting of Si and Ru is formed, a reflectance is decreased due to the interdiffusion layer 21b. Further, when the multilayer reflection film is heated in mask processing or in exposure by EUV light using a mask, the interdiffusion layer consisting of Si and Ru becomes thicker, or the interdiffusion layer consisting of Si and Ru changes in its nature. Further, when the protection layer composed of a material containing Ru is exposed to the air, not only the protection layer but also the Si layer is oxidized, resulting in a further decrease of reflectance.

On the other hand, as shown in FIG.1, when the Mo layer 212 in the Si/Mo laminated portion 21 is contacted to the protection layer 22, the interdiffusion layer consisting of Si and Ru that causes decrease of reflectance is not formed between the Si/Mo laminated portion and the protection layer composed of a material containing Ru. Thus, a high reflectance is achieved in compared with the case in which the Si layer in the Si/Mo laminated portion is contacted to the protection layer.

When the Mo layer in the Si/Mo laminated portion is contacted to the protection layer, the layer containing Si and N is preferably formed between the closest Si layer, and the Mo layer contacted to the protection layer, and in contact with both of the Si layer and the Mo layer. In particular, the uppermost part of the multilayer reflection film preferably consists of, from the side remote from the substrate, the protection layer, the Mo layer, the layer containing Si and N, and the Si layer. The portion between the Si layer closest to the Mo layer in the Si/Mo laminated portion contacted to the protection layer, and the Mo layer contacted to the protection layer is easily affected by the protection layer. Further, when the multilayer reflection film is heated, this portion is most susceptible to the influence of heat, so this portion has highest potential for generating the interdiffusion layer composed of Si and Mo. Therefore, it is particularly effective for obtaining a high reflectance that the layer containing Si and N is formed between the Si layer and the Mo layer in the uppermost part of the multilayer reflection film.

In this case, by forming the layer containing Si and N, even when the Mo layer contacted to the protection layer composed of a material containing Ru is formed thin, the protection layer composed of a material containing Ru becomes a stable state having a crystalline dense structure by forming the protection layer composed of a material
5 containing Ru on the Mo layer even when the protection layer composed of a material containing Ru is comparatively thin. Therefore, a thickness of the Mo layer contacted to the protection layer composed of a material containing Ru is preferably not more than 2 nm, more preferably not more than 1 nm. Particularly, when the uppermost part of the multilayer reflection film consists of, from the side remote from the substrate, the
10 protection layer, the Mo layer, the layer containing Si and N, and the Si layer, the protection layer preferably has a thickness of not more than 4 nm, the Mo layer preferably has a thickness of not more than 1 nm, the layer containing Si and N preferably has a thickness of not more than 2 nm, and the Si layer preferably has a thickness of not more than 4 nm.

15 In the invention, with respect to a reflectance of the multilayer reflection film, the multilayer reflection film may have 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°. Even if the multilayer reflection film is heat-treated, for example, in the air at 200 °C for 10 minutes, the change (decrease) of the reflectance is small, and even after the heat treatment,
20 the peak reflectance can be maintained in the range of not less than 65%.

Examples of methods for forming the Si/Mo laminated portion include a sputtering method in which, to perform sputtering, power is supplied to a target, and plasma of an atmospheric gas is formed (an atmospheric gas is ionized) by the supplied power, and an ion beam sputtering method in which a target is irradiated with ion beam. The sputtering
25 methods include a DC sputtering method in which a DC voltage is applied to a target, and an RF sputtering method in which a high frequency voltage is applied to a target. The sputtering method is a film forming method that utilizes sputtering phenomenon of gas ions by applying a voltage to a target with feeding a sputter gas into a chamber to ionize the gas. Particularly, a magnetron sputtering method has an advantage in productivity. The power
30 may be applied to the target by a DC system or an RF system. The DC system also includes a pulse sputtering that inverts a negative bias applied to the target for a short time in order to prevent charge-up of the target.

The Si/Mo laminated portion can be formed by a sputtering method using a sputtering apparatus to which a plurality of targets can be attached. The Si layer, the layer containing Si and N, and the Mo layer can be sequentially formed in sequential sputtering of a silicon (Si) target and a molybdenum (Mo) target. In particular, these layers may be
5 formed by using the silicon (Si) target for forming the Si layer and the layer containing Si and N, and the molybdenum (Mo) target for forming the Mo layer; using, as a sputter gas, rare gas such as helium (He) gas, argon (Ar) gas, krypton (Kr) gas and xenon (Xe) gas in the case of forming the Si layer or the Mo layer, or the rare gas with a nitrogen-containing gas such as nitrogen gas (N₂) gas in the case of forming the layer containing Si and N; and
10 disposing the substrate and each of the targets in offset arrangement in which the vertical line passing through the center of the sputtering surface of each target does not match with the vertical line passing through the center of the film forming surface of the substrate. The sputtering is preferably performed while rotating the substrate along its main surface. Further, in this case, it is preferable that none of shield members such as shutters which
15 shield between the substrate and the target are disposed. In addition, the layer containing Si and N may be formed by a reactive sputtering using a nitrogen-containing gas, or by using a silicon compound target such as silicon nitride target as the target.

The Si/Mo laminated portion can be formed by a method including step (A): forming the Si/Mo laminated portion by sputtering. In this case, the sputtering is
20 preferably performed by a magnetron sputtering apparatus including a chamber. Preferably, in this chamber, one or more Mo targets and one or more Si targets are attachable; powers are individually applicable 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
25 rotatable along its main surface; and nitrogen-containing gas is introducible.

The protection layer can be formed by, for example, a sputtering method such as an ion beam sputtering and a magnetron sputtering, as same in the case of the Si/Mo laminated portion. However, a magnetron sputtering method has an advantage, as same in the case of the Si/Mo laminated portion.

30 The protection layer can be formed by a sputtering method using a sputtering apparatus to which a single target or a plurality of targets can be attached. In particular, the protection layer is formed by using a ruthenium (Ru) target and an optional target

composed of at least one element selected from the group consisting of niobium (Nb) and zirconium (Zr); using, as a sputter gas, a rare gas such as helium (He) gas, argon (Ar) gas, krypton (Kr) gas and xenon (Xe) gas; and disposing the main surface of the substrate so as to face to the target (for example, disposing the main surface of the substrate in

5 arrangement in which the vertical line passing through the center of the sputtering surface of the target matches with the vertical line passing through the center of the film forming surface of the substrate) and sputtering a single target, or disposing the substrate and each of the targets in offset arrangement and sputtering multiple targets simultaneously. The sputtering is preferably performed while rotating the substrate along its main surface.

10 When the protection layer is formed by a compound containing another element other than metal, the protection layer can be formed by reactive sputtering using, as a sputter gas, a reactive gas such as an oxygen-containing gas, a nitrogen-containing gas and a carbon containing gas together with a rare gas. Further, a target composed of a compound may also be used.

15 In this way, the multilayer reflection film can be suitably formed by the step (A): forming the Si/Mo laminated portion by sputtering, and the step (B): forming the protection layer by sputtering. In this case, for example, the step (A) is performed in one sputter chamber, the substrate on which the Mo/Si laminated portion has been formed is transferred from the one sputter chamber to the other sputter chamber, and then, the step
20 (B) is performed in the other sputter chamber. However, if the Si/Mo laminated portion is exposed in, for example, an atmosphere containing oxygen such as the air, an unnecessary oxide layer is formed at the portion between the Si/Mo laminated portion and the protection layer, resulting decrease of reflectance and causing peel at the portion of them in some cases. Therefore, when shifting to the step (B) after the step (A), it is preferable that
25 none of gases reactable to the Mo/Si laminated portion, particularly none of oxygen-containing gases such as oxygen gas (O₂ gas) are contacted to the Mo/Si laminated portion that has been formed in the step (A), in particular, without exposing the Mo/Si laminated portion to the air until shifting to the step (B), then the step (B) is performed.

30 When the step (A) is performed in one sputter chamber, and the substrate on which the Mo/Si laminated portion has been formed is transferred from the one sputter chamber to the other sputter chamber, and then the step (B) is performed in the other sputter chamber, as a method for performing the step (B) without contacting the Si/Mo laminated

portion formed in the step (A) with gases which are reactable to the Mo/Si laminated portion, examples of the method include a method in which a transfer chamber capable of communicating with each of the sputter chambers individually or with both of the sputter chambers at the same time is provided between the one and other sputter chambers, and in
5 which the substrate on which the Mo/Si laminated portion has been formed is transferred from the one sputter chamber via the transfer chamber to the other sputter chamber. At this time, both of the transfer from the one sputter chamber to the transfer chamber and the transfer from the transfer chamber to the other sputter chamber are preferably performed under an inert gas atmosphere at a normal pressure (atmospheric pressure) or a reduced
10 pressure (lower pressure than normal pressure), or under vacuum.

FIG. 4 is a conceptual diagram showing an example of a sputtering apparatus suitable for forming a multilayer reflection film of the invention. The sputtering apparatus 100 is configured by a sputter chamber 101 for forming the Si/Mo laminated portion by sputtering, a sputter chamber 102 for forming the protection layer by sputtering,
15 a transfer chamber 103 communicating with each of the sputter chambers 101, 102, and a load lock chamber 104 communicating with the transfer chamber 103. An openable and closable bulkhead (not shown) is provided between the transfer chamber 103 and the load lock chamber 104. Further, an openable and closable bulkhead is optionally provided between each of the sputter chambers 101, 102 and the transfer chamber 103.

20 When the multilayer reflection film is formed by such a sputtering apparatus, for example, first, a substrate is introduced into the load lock chamber 104, the pressure inside the load lock chamber 104 is reduced, the bulkhead is opened, the substrate is transferred via the transfer chamber 103 to the sputter chamber 101, then, the Si / Mo laminated portion is formed in the sputter chamber 101. Next, the substrate on which the Si / Mo laminated
25 portion has been formed is transferred from the sputter chamber 101 via the transfer chamber 103 to the sputter chamber 102, then the protection layer is formed in the sputter chamber 102. Next, the substrate on which the Si / Mo laminated portion and the protection layer (multilayer reflection film) has been formed is transferred from the sputter chamber 102 via the transfer chamber 103 to the load lock chamber 104, the bulkhead is
30 closed, the pressure of inside of the road lock chamber 104 is returned to normal pressure, then the substrate on which the multilayer reflection film is formed is taken out. By such a way, a substrate with a multilayer reflection film for an EUV mask blank can be obtained.

When the multilayer reflection film is formed in this way, the step (B) can be performed without contacting the Si/Mo laminated portion formed in the step (A) with gases which are reactable to the Mo/Si laminated portion.

To manufacture an EUV mask blank, an absorber film is formed on the multilayer reflection film of the substrate with a multilayer reflection film for an EUV mask blank.

The EUV mask blank of the invention includes an absorber film that is formed on the multilayer reflection film of the substrate with a multilayer reflection film for an EUV mask blank, and absorbs exposure light, specifically, an absorber film that absorbs EUV light and reduces a reflectance. The absorber film is preferably formed in contact with the protection layer. The EUV mask blank may further include, on the absorber film, a hard mask film that acts as an etching mask for dry etching the absorber film. On the other hand, a conductive film may be formed on the other main surface (back side surface) of the substrate which is the opposite side to the one main surface, preferably in contact with the substrate. The conductive film is used for holding an EUV mask on an exposure tool by an electrostatic chuck. In the invention, one main surface of the substrate is defined as the front side or the upper side, and the other main surface is defined as the back side or the lower side. However, the front and back sides or the upper and lower sides in both surfaces are defined for the sake of convenience. Two main surfaces (film forming surfaces) are one and the other main surfaces, respectively. The front and back sides or the upper and lower sides may be substituted.

From the EUV mask blank (a mask blank for EUV exposure), an EUV mask (a mask for EUV exposure) including an absorber pattern (a pattern of the absorber film) formed by patterning the absorber film is manufactured. The EUV mask blank and the EUV mask are a reflective mask blank and a reflective mask, respectively.

The absorber film is formed on the multilayer film, and is a film that absorbs EUV light as an exposure light and reduces reflectance of the exposure light. A transfer pattern in an EUV mask is formed by a difference of reflectance between a portion on which the absorber film is formed and a portion on which the absorber film is not formed.

A material of the absorber film is not limited as long as a material can absorb EUV light and is processible to a pattern. Examples of the material of the absorber film include, for example, a material containing tantalum (Ta) or chromium (Cr). The material containing Ta or Cr may contain oxygen (O), nitrogen (N), carbon (C), boron (B), or other

elements. Examples of the material containing Ta include, for example, Ta simple substance, and a tantalum compound such as TaO, TaN, TaON, TaC, TaCN, TaCO, TaCON, TaB, TaOB, TaNB, TaONB, TaCB, TaCNB, TaCOB and TaCONB. Examples of the material containing Cr include, for example, Cr simple substance, and a chromium compound such as CrO, CrN, CrON, CrC, CrCN, CrCO, CrCON, CrB, CrOB, CrNB, CrONB, CrCB, CrCNB, CrCOB and CrCONB.

The absorber film can be formed by a sputtering method, and the sputtering is preferably a magnetron sputtering. In particular, the absorber film is formed by using a metal target such as a chromium (Cr) target and a tantalum (Ta) target or a metal compound target such as a chromium compound target and a tantalum compound target (a target containing a metal such as Cr and Ta, and at least one selected from the group consisting of oxygen (O), nitrogen (N), carbon (C), boron (B) and the like); and using, as a sputter gas, a rare gas such as helium (He) gas, argon (Ar) gas, krypton (Kr) gas and xenon (Xe) gas in sputtering, or using the rare gas with a reactive gas such as an oxygen-containing gas, a nitrogen-containing gas and a carbon-containing gas in a reactive sputtering.

On the side of absorber film that is remote from the substrate, a hard mask film (an etching mask film for the absorber film) having different etching properties from the absorber film may be provided preferably in contact with the absorber film. The hard mask film is a film that acts as an etching mask when an absorber film is etched by dry etching. After the absorber pattern is formed, the hard mask film may be left as the reflectance reducing film for reducing the reflectance at the wavelength of light used in inspections such as pattern inspection as a part of the absorber film, or removed to be absent on the reflective mask. Examples of the material of the hard mask film include a material containing chromium (Cr). A hard mask film composed of a material containing Cr is more preferable in case that the absorber film is composed of a material containing Ta and free of Cr. When a layer that mainly has a function for reducing the reflectance at the wavelength of light used in inspection such as pattern inspection (the reflectance reducing layer) is formed on the absorber film, the hard mask film may be formed on the reflectance reducing film of the absorber film. The hard mask film may be formed by, for example, a magnetron sputtering method. A thickness of the hard mask is normally about 5 to 20 nm, however, not limited thereto.

A sheet resistance of the conductive film is preferably not more than $100 \Omega/\square$, and a material of the conductive film are not particularly limited. Examples of the material of the conductive film include, for example, a material containing tantalum (Ta) or chromium (Cr). The material containing Ta or Cr may contain oxygen (O), nitrogen (N), carbon (C), boron (B), or other elements. Examples of the material containing Ta include, for example, Ta simple substance, and a tantalum compound such as TaO, TaN, TaON, TaC, TaCN, TaCO, TaCON, TaB, TaOB, TaNB, TaONB, TaCB, TaCNB, TaCOB and TaCONB. Examples of the material containing Cr include, for example, Cr simple substance, and a chromium compound such as CrO, CrN, CrON, CrC, CrCN, CrCO, CrCON, CrB, CrOB, CrNB, CrONB, CrCB, CrCNB, CrCOB and CrCONB.

A thickness of the conductive film is not particularly limited as long as the conductive film has a function for an electrostatic chuck use. The thickness is normally about 5 to 100 nm. The thickness of the conductive film is preferably formed so that a film stress is balanced with the multilayer reflection film and the absorber pattern after an EUV mask is obtained, that is, after the absorber pattern is formed. The conductive film may be formed before forming the multilayer reflection film, or after forming all of the films disposed at the side of the multilayer reflection film on the substrate. Further, the conductive film may be formed after forming a part of the films disposed at the side of the multilayer reflection film on the substrate, and then the remainder of the films disposed at the side of the multilayer reflection film on the substrate may be formed. The conductive film may be formed by, for example, a magnetron sputtering method.

Further, the EUV mask blank may include a resist film formed on the side remotest from the substrate. The resist film is preferably an electron beam (EB) resist.

EXAMPLES

Examples of the invention are given below by way of illustration and not by way of limitation.

Example 1

A multilayer reflection film consisting of a Si/Mo laminated portion and a protection layer containing Ru was formed on a substrate. The substrate was composed of a low thermal expansion material having a coefficient of thermal expansion within the

range of $\pm 5.0 \times 10^{-9} / ^\circ\text{C}$, a surface roughness of the main surface of not more than 0.1 nm in RMS value, and a flatness of the main surface of 100 nm in TIR value.

The Si/Mo laminated portion was formed by magnetron sputtering using a Si target and a Mo target as targets, and Ar gas and N₂ gas as sputter gases. One Si target and one Mo target were attached to a magnetron sputtering apparatus, the substrate and each target were arranged in an offset arrangement, and the substrate was rotated. First, a Si layer was formed at a setting thickness of 3.0 nm by introducing only Ar gas into a sputter chamber, and discharging only the Si target. Next, a SiN layer was formed at a setting thickness of 1.0 nm by introducing Ar gas and N₂ gas into the sputter chamber, and discharging only the Si target. Next, a Mo layer was formed at a setting thickness of 3.0 nm by introducing only Ar gas into the sputter chamber, and discharging only the Mo target. A cycle of the formations of these three layers, the Si layer, the SiN layer and the Mo layer, as one cycle, was repeated for a total of 40 cycles. Then, a Si layer was formed at a setting thickness of 2.8 nm by introducing only Ar gas into the sputter chamber, and discharging only the Si target. Next, a SiN layer was formed at a setting thickness of 1.0 nm by introducing Ar gas and N₂ gas into the sputter chamber, and discharging only the Si target. Next, a Mo layer was formed at a setting thickness of 0.5 nm by introducing only Ar gas into the sputter chamber, and discharging only the Mo target.

The protection layer was formed by magnetron sputtering using a Ru target as a target, and Ar gas as a sputter gas. One Ru target was attached to another magnetron sputtering apparatus which differs from the magnetron sputtering apparatus used for forming the Si/Mo laminated portion, the substrate was faced to the target, and the substrate was rotated. The substrate on which the Si/Mo laminated portion has been formed was transferred under vacuum from the magnetron sputtering apparatus used for forming the Si/Mo laminated portion to the other magnetron sputtering apparatus used for forming the protection layer via a transfer chamber that communicates with both sputter chambers. A Ru layer was formed at a setting thickness of 2.5 nm by introducing Ar gas into the sputter chamber, and discharging the Ru target, obtaining the protection layer.

When the cross section of the obtained multilayer reflection film was observed by a transmission electron microscope (TEM), from the surface side (the side remote from the substrate), a Ru layer having a thickness of 2.5 nm, a Mo layer having a thickness of 0.5 nm, a SiN layer having a thickness of 1.0 nm, a Si layer having a thickness of 2.6 nm, an

interdiffusion layer having a thickness of 0.5 nm in which Si and Mo are mixed, a Mo layer having a thickness 2.3 nm, and a SiN layer having a thickness of 0.9 nm were observed in this order at the upper portion of the multilayer reflection film. Further, the multilayer reflection film obtained by the same method was heat-treated at 200 °C for 10 minutes in air atmosphere. When the cross section of the multilayer reflection film was observed in the same manner, the observed multilayer reflection film was similar to that not heat-treated. Further, when a peak reflectance of EUV light in the wavelength range of 13.4 to 13.6 nm at an incident angle of 6 ° was measured before and after the heat treatment. The results were 67% before the heat treatment and 65% after the heat treatment that satisfy a high reflectance of not less than 65%.

Example 2

A multilayer reflection film consisting of a Si/Mo laminated portion and a protection layer containing Ru was formed on a substrate. The substrate was composed of a low thermal expansion material having a coefficient of thermal expansion within the range of $\pm 5.0 \times 10^{-9}/^{\circ}\text{C}$, a surface roughness of the main surface of not more than 0.1 nm in RMS value, and a flatness of the main surface of 100 nm in TIR value.

The Si/Mo laminated portion was formed by magnetron sputtering using a Si target and a Mo target as targets, and Ar gas and N₂ gas as sputter gases. One Si target and one Mo target were attached to a magnetron sputtering apparatus, the substrate and each target were arranged in an offset arrangement, and the substrate was rotated. First, a Si layer was formed at a setting thickness of 3.0 nm by introducing only Ar gas into a sputter chamber, and discharging only the Si target. Next, a SiN layer was formed at a setting thickness of 0.5 nm by introducing Ar gas and N₂ gas into the sputter chamber, and discharging only the Si target. Next, a Mo layer was formed at a setting thickness of 3.0 nm by introducing only Ar gas into the sputter chamber, and discharging only the Mo target. Next, a SiN layer was formed at a setting thickness of 0.5 nm by introducing Ar gas and N₂ gas into the sputter chamber, and discharging only the Si target. A cycle of the formations of these four layers, the Si layer, the SiN layer, the Mo layer and the SiN layer, as one cycle, was repeated for a total of 40 cycles. Then, a Si layer was formed at a setting thickness of 2.4 nm by introducing only Ar gas into the sputter chamber, and discharging only the Si target. Next, a SiN layer was formed at a setting thickness of 0.5

nm by introducing Ar gas and N₂ gas into the sputter chamber, and discharging only the Si target. Next, a Mo layer was formed at a setting thickness of 0.5 nm by introducing only Ar gas into the sputter chamber, and discharging only the Mo target.

5 The protection layer was formed by magnetron sputtering using a Ru target as a target, and Ar gas as a sputter gas. One Ru target was attached to another magnetron sputtering apparatus which differs from the magnetron sputtering apparatus used for forming the Si/Mo laminated portion, the substrate was faced to the target, and the substrate was rotated. The substrate on which the Si/Mo laminated portion has been formed was transferred under vacuum from the magnetron sputtering apparatus used for forming the Si/Mo laminated portion to the other magnetron sputtering apparatus used for forming the protection layer via a transfer chamber that communicates with both sputter chambers. A Ru layer was formed at a setting thickness of 2.5 nm by introducing Ar gas into the sputter chamber, and discharging the Ru target, obtaining the protection layer.

15 When the cross section of the obtained multilayer reflection film was observed by a transmission electron microscope (TEM), from the surface side (the side remote from the substrate), a Ru layer having a thickness of 2.7 nm, a Mo layer having a thickness of 0.5 nm, a SiN layer having a thickness of 0.5 nm, a Si layer having a thickness of 2.5 nm, a SiN layer having a thickness of 0.5 nm, a Mo layer having a thickness 2.5 nm, and a SiN layer having a thickness of 0.5 nm were observed in this order at the upper portion of the multilayer reflection film. Further, the multilayer reflection film obtained by the same method was heat-treated at 200 °C for 10 minutes in air atmosphere. When the cross section of the multilayer reflection film was observed in the same manner, the observed multilayer reflection film was similar to that not heat-treated. Further, when a peak reflectance of EUV light in the wavelength range of 13.4 to 13.6 nm at an incident angle of 6 ° was measured before and after the heat treatment. The results were 67% before the heat treatment and 65% after the heat treatment that satisfy a high reflectance of not less than 65%.

Comparative Example 1

30 A multilayer reflection film consisting of a Si/Mo laminated portion and a protection layer containing Ru was formed on a substrate. The substrate was composed of a low thermal expansion material having a coefficient of thermal expansion within the

range of $\pm 5.0 \times 10^{-9} / ^\circ\text{C}$, a surface roughness of the main surface of not more than 0.1 nm in RMS value, and a flatness of the main surface of 100 nm in TIR value.

The Si/Mo laminated portion was formed by magnetron sputtering using a Si target and a Mo target as targets, and Ar gas as a sputter gas. One Si target and one Mo target were attached to a magnetron sputtering apparatus, the substrate and each target were arranged in an offset arrangement, and the substrate was rotated. First, a Si layer was formed at a setting thickness of 4.0 nm by introducing Ar gas into a sputter chamber, and discharging only the Si target. Next, a Mo layer was formed at a setting thickness of 3.0 nm by introducing Ar gas into the sputter chamber, and discharging only the Mo target. A cycle of the formations of these two layers, the Si layer and the Mo layer, as one cycle, was repeated for a total of 40 cycles. Then, a Si layer was formed at a setting thickness of 3.0 nm by introducing Ar gas into the sputter chamber, and discharging only the Si target. Next, a Mo layer was formed at a setting thickness of 1.0 nm by introducing Ar gas into the sputter chamber, and discharging only the Mo target.

The protection layer was formed by magnetron sputtering using a Ru target as a target, and Ar gas as a sputter gas. One Ru target was attached to another magnetron sputtering apparatus which differs from the magnetron sputtering apparatus used for forming the Si/Mo laminated portion, the substrate was faced to the target, and the substrate was rotated. The substrate on which the Si/Mo laminated portion has been formed was transferred under vacuum from the magnetron sputtering apparatus used for forming the Si/Mo laminated portion to the other magnetron sputtering apparatus used for forming the protection layer via a transfer chamber that communicates with both sputter chambers. A Ru layer was formed at a setting thickness of 2.5 nm by introducing Ar gas into the sputter chamber, and discharging the Ru target, obtaining the protection layer.

When the cross section of the obtained multilayer reflection film was observed by a transmission electron microscope (TEM), from the surface side (the side remote from the substrate), a Ru layer having a thickness of 2.5 nm, an interdiffusion layer having a thickness of 1.2 nm in which Si and Mo are mixed, a Si layer having a thickness of 2.8 nm, an interdiffusion layer having a thickness of 0.5 nm in which Si and Mo are mixed, a Mo layer having a thickness 2.7 nm, and an interdiffusion layer having a thickness of 1.3 nm in which Si and Mo are mixed were observed in this order at the upper portion of the multilayer reflection film. Further, the multilayer reflection film obtained by the same

method was heat-treated at 200 °C for 10 minutes in air atmosphere. When the cross section of the multilayer reflection film was observed in the same manner, from the surface side (the side remote from the substrate), a Ru layer having a thickness of 2.5 nm, an interdiffusion layer having a thickness of 1.6 nm in which Si and Mo are mixed, a Si layer
5 having a thickness of 2.6 nm, an interdiffusion layer having a thickness of 0.5 nm in which Si and Mo are mixed, a Mo layer having a thickness of 2.6 nm, and an interdiffusion layer having a thickness of 1.6 nm in which Si and Mo are mixed were observed in this order at the upper portion of the multilayer reflection film. Further, when a peak reflectance of EUV light in the wavelength range of 13.4 to 13.6 nm at an incident angle of 6 ° was
10 measured before and after the heat treatment. The results were 65% before the heat treatment and 62% after the heat treatment, and the reflectance was a low reflectance of less than 65% in the case after the heat treatment.

CLAIMS:

1. A substrate with a multilayer reflection film for an EUV mask blank comprising a
5 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 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
10 and the Mo layer.
2. The substrate of claim 1, wherein the layer containing Si and N has a thickness of
not more than 2 nm.
- 15 3. The substrate of claim 1 or 2, wherein the multilayer reflection film further
comprises a protection layer containing Ru formed in contact with the Si/Mo laminated
portion, as the uppermost layer.
4. The substrate of claim 3, wherein the protection layer is contact with the Mo layer
20 of the Si/Mo laminated portion.
5. The substrate of claim 4, 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.
- 25 6. The substrate of claim 5, 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.

30

7. The substrate of any one of claims 1 to 6, 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,
- 5 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.
8. The substrate of any one of claims 1 to 6, wherein the Si/Mo laminated portion
- 10 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.
- 15 9. The substrate of any one of claims 1 to 8, 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°.
10. A manufacturing method for the substrate with a multilayer reflection film for an
- 20 EUV mask blank of any one of claims 1 to 9, 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;
- 25 powers are individually applicable 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.
- 30
11. A manufacturing method for the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 3 to 6, the method comprising the steps of

(A) forming the Si/Mo laminated portion by sputtering, and
(B) forming the protection layer by sputtering, wherein
after the step (A), the Mo/Si laminated portion is provided to the step (B) without
contacting to gases reactable to the Mo/Si laminated portion that has been formed in the
5 step (A).

12. The manufacturing method of claim 11, wherein the step (A) is performed in one
sputter chamber, the substrate on which the Mo/Si laminated portion has been formed is
transferred to the other sputter chamber, and then, the step (B) is performed in the other
10 sputter chamber.

13. The manufacturing method of claim 12, wherein a transfer chamber is provided
between said one and other sputter chambers, the transfer chamber is capable of
communicating with each of the sputter chambers individually or with both of the sputter
15 chambers at the same time, and the substrate on which the Mo/Si laminated portion has
been formed is transferred from said one sputter chamber via the transfer chamber to said
other sputter chamber.

14. The manufacturing method of claim 13, wherein the substrate is transferred under
20 vacuum both in the transfer from said one sputter chamber to the transfer chamber, and the
transfer from the transfer chamber to said other sputter chamber.

15. The manufacturing method of any one of claims 11 to 14, wherein the Si/Mo
laminated portion comprises not less than 30 of three-layer laminated structure units, and
25 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.

30

16. The manufacturing method of any one of claims 11 to 14, 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.

5

17. The manufacturing method of any one of claims 11 to 16, 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°.

10 18. An EUV mask blank comprising the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 1 to 9, and an absorber film containing Ta or Cr formed on the multilayer reflection film.

15 19. An EUV mask blank comprising the substrate with a multilayer reflection film for an EUV mask blank of any one of claims 1 to 9, 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.