

DESCRIPTION

Title of Invention: REFLECTIVE MASK AND METHOD FOR
PRODUCING REFLECTIVE MASK

5

Technical Field

[0001]

The present disclosure relates to a reflective mask
and a method for producing a reflective mask.

10

Background Art

[0002]

Conventionally, reflective masks which have enabled
the miniaturization by photolithography by using an EUV
15 exposure device using a short-wavelength EUV light have
posed a problem referred to as a so-called "shadowing
effect" in which the optical axis is tilted when the EUV
light is incident, and therefore the incident EUV light
creates a shadow of a photomask pattern (absorption film
20 pattern), which deteriorates the transfer performance.

To address the problem, a reflective mask has been
proposed which reduces the shadowing effect by enabling
the formation of an absorption film having a film
thickness smaller than before by using a material having
25 a high extinction coefficient k for the absorption film
and suppressing the EUV reflectance (See PTL 1, for
example).

Citation List

Patent Literature

[0003]

PTL 1: WO 2018/159785

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Summary of Invention

Technical Problem

[0004]

10 In the EUV exposure device, cleaning with hydrogen radicals is performed to prevent contamination inside a chamber due to contamination (mixing of impurities). More specifically, the reflective mask needs to be formed using materials resistant to hydrogen radical reduction. However, some materials having a high extinction

15 coefficient k have low hydrogen radical resistance, which has posed a problem that reflective masks formed of the materials having low hydrogen radical resistance cannot withstand long-term use.

[0005]

20 It is an object of the present disclosure to provide a reflective mask capable of reducing the shadowing effect and having sufficient hydrogen radical resistance and a method for producing the reflective mask.

25 Solution to Problem

[0006]

To solve the above-described problems, a reflective mask according to one aspect of the present disclosure

includes: a substrate; a reflective film reflecting an EUV light having a multi-layer film structure formed on the substrate; a protective film formed on the reflective film, and protecting the reflective film; an absorption
5 film absorbing the EUV light formed on the protective film; and an oxide coating formed on the absorption film; in which the absorption film contains Sn and a metal element other than Sn and has a ratio of the atomic weight of the Sn to the total atomic weight of the metal
10 element other than Sn (Sn/Metal element other than Sn) within the range of 1 or more and less than 20, and the oxide coating is resistant to a hydrogen radical and formed on the surface and the side surfaces of the absorption film.

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Advantageous Effects of Invention

[0007]

One aspect of the present disclosure can provide a reflective mask capable of reducing the shadowing effect
20 and having sufficient hydrogen radical resistance and a method for producing the reflective mask.

Brief Description of Drawings

[0008]

25 FIG. 1 is a cross-sectional view schematically illustrating one configuration example of a reflective mask according to this embodiment;

FIG. 2 is a graph showing the optical constant of

each metal at the wavelength of an EUV light;

FIG. 3 is a conceptual view illustrating a method for evaluating hydrogen radical resistance according to this embodiment;

5 FIG. 4 is a schematic cross-sectional view illustrating a step of producing a reflective mask according to this embodiment;

FIG. 5 is a schematic cross-sectional view illustrating a step of producing the reflective mask
10 according to this embodiment;

FIG. 6 is a schematic cross-sectional view illustrating a step of producing the reflective mask according to this embodiment;

FIG. 7 is a schematic cross-sectional view
15 illustrating a step of producing the reflective mask according to this embodiment; and

FIG. 8 is a schematic cross-sectional view illustrating a step of producing the reflective mask according to this embodiment.

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Description of Embodiments

[0009]

One embodiment of the present disclosure will now be described with reference to the drawings.

25 Herein, the drawings are schematic, and the relationship between the thickness and the plane dimension, the thickness ratio of each layer, and the like are different from the actual relationship, ratio,

and the like. The embodiment described below exemplifies configurations for embodying the technical idea of the present disclosure. The technical idea of the present disclosure does not specify materials, shapes, structures, and the like of constituent components to the materials, shapes, structures, and the like described below. The technical idea of the present disclosure can be variously altered within the technical range defined by Claims.

10 [0010] (Configuration of reflective mask)

The basic configuration of a reflective mask according to one embodiment of the present disclosure is described using FIG. 1. FIG. 1 is a cross-sectional view for describing one configuration example of a reflective photomask (reflective mask) 100 according to the embodiment of the present disclosure.

As illustrated in FIG. 1, the reflective photomask 100 according to one embodiment of the present disclosure has a multi-layer reflective film 12, a protective film 13, and an absorption film pattern 14a deposited in this order on one surface side of a substrate 11. The absorption film pattern 14a is formed by patterning an absorption film 14 described later. Further, an oxide coating 15 is formed on the surface and the side surfaces of the absorption film pattern 14a. Hereinafter, each layer is described in detail.

[0011] (Substrate)

The substrate 11 is a layer serving as a base of the

reflective photomask 100. For the substrate 11 according to this embodiment, a flat Si substrate, synthetic quartz substrate, or the like is usable. Further, a low thermal expansion glass to which titanium is added is usable for
5 the substrate 11. However, this embodiment is not limited to the above insofar as materials have a small thermal expansion coefficient.

As illustrated in FIG. 8, a back surface conductive film 16 can be formed on the surface on which the multi-
10 layer reflective film 12 is not formed of the substrate 11. The back surface conductive film 16 is a film for fixing the reflective photomask 100 utilizing the principle of an electrostatic chuck when the reflective photomask 100 is installed in an exposure machine.

15 [0012] (Multi-layer reflective film)

The multi-layer reflective film 12 is a layer having a multi-layer film structure formed on the substrate 11 and is a layer provided to reflect an EUV light (extreme ultraviolet light) which is an exposure light in the
20 reflective photomask 100.

The multi-layer reflective film 12 contains a plurality of reflective films containing a combination of materials having greatly different refractive indices to the EUV light. For example, the multi-layer reflective
25 film 12 can be formed by repeatedly depositing a layer containing a combination of Mo (molybdenum) and Si (silicon) or Mo (molybdenum) and Be (beryllium) by about 40 cycles.

[0013] (Protective film)

The protective film 13 is a layer formed on the multi-layer reflective film 12 and is a layer functioning as an etching stopper to prevent damage to the multi-layer reflective film 12 in forming the absorption film pattern 14a by etching. The protective film 13 may not be provided depending on materials of the multi-layer reflective film 12 and etching conditions. The protective film 13 according to this embodiment is formed of a material resistant to dry etching performed in pattern formation of an absorption film 14.

[0014] (Absorption film)

The absorption film 14 is a layer formed on the protective film 13 and is a layer absorbing the EUV light which is an exposure light in the reflective photomask 100. The absorption film 14 is a layer forming an absorption layer pattern (transfer pattern) which is a fine pattern for transfer.

[0015]

As illustrated in FIG. 1, an absorption pattern (absorption film pattern 14a) of the reflective photomask 100 is formed by removing a part of the absorption film 14 of a reflective photomask blank, i.e., patterning the absorption film 14. In the EUV lithography, the EUV light is obliquely incident and reflected by the multi-layer reflective film 12, but the transfer performance onto a wafer (semiconductor substrate) sometimes deteriorates due to a shadowing effect in which the

absorption film pattern 14a interferes with an optical path. This deterioration of the transfer performance is reduced by reducing the thickness of the absorption film pattern 14a absorbing the EUV light. The thickness of
5 the absorption film pattern 14a can be reduced by applying a material having higher absorptivity to the EUV light than that of a conventional material, i.e., a material having a high extinction coefficient k to a wavelength of 13.5 nm.

10 [0016]

FIG. 2 is a graph showing the optical constant to the wavelength of 13.5 nm of the EUV light of each metal material. The horizontal axis of FIG. 2 represents the refractive index n and the vertical axis represents the
15 extinction coefficient k . The extinction coefficient k of tantalum (Ta), which is a main material of the conventional absorption film 14, is 0.041. Compound materials having the extinction coefficient k larger than that of tantalum (Ta) can reduce the thickness of the
20 absorption film 14 as compared with conventional compound materials. By the use of materials having the extinction coefficient k of 0.06 or more as the main ingredient, the thickness of the absorption film 14 can be sufficiently reduced, and thus the shadowing effect can be reduced.

25 [0017]

As materials satisfying a combination of the optical constants (nk value) described above, silver (Ag), indium (In), tin (Sn), nickel (Ni), tellurium (Te), and the like

are present, for example, and their extinction coefficients k are within the range of 0.07 to 0.08 as illustrated in FIG. 2. In the case of the materials above, the extinction coefficients k can be significantly increased to about twice the extinction coefficient 0.041 of tantalum (Ta), which is a conventional absorption film material, and therefore high light absorptivity is obtained. However, most of these materials having high light absorptivity are difficult to be processed into a reflective mask due to poor dry etching properties (in other words, halides of these elements have low volatility), and thus have poor practicality as a reflective mask. In contrast to these materials, Sn, which has the high extinction coefficient k , is an absorption film material having a high dry etching rate with respect to a fluorine-based gas or a chlorine-based gas and having good processability. In an EUV exposure device provided with a reflective photomask, when the photomask is exposed to a hydrogen radical environment, a simple Sn substance reacts with the hydrogen radicals and is converted to gaseous SnH_4 , which causes a film reduction of the absorption film pattern 14a. As a countermeasure against the above, the life of the photomask can be prolonged by covering the surface and the side surfaces of the absorption film pattern 14a with the oxide coating 15 described later.

[0018]

For the absorption film 14, compound materials

containing Sn and a metal element M other than Sn are usable. The absorption film 14 preferably has a ratio of the atomic weight of Sn, which is the main ingredient, to the total atomic weight of the metal element M other than Sn (hereinafter also simply referred to as "Sn/M") of 1 or more. When Sn/M in the absorption film 14 is 1 or more, the shadowing effect can be reduced and the transfer performance can be improved. In this embodiment, the "main ingredient" means an element (ingredient) having the largest content ratio among elements (ingredients) constituting the absorption film 14.

[0019]

Further, for the absorption film 14, compound materials containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf are usable as the metal element M other than Sn. The mixing ratio of these compounds needs to be a mixing ratio at which the oxide coating 15 having hydrogen radical resistance is stably formed. Therefore, the mixing ratio of the compound materials (metal element M other than Sn) in the absorption film 14 needs to be less than 20 at maximum in terms of the Sn/M ratio above. More specifically, Sn/M in the absorption film 14 is desirably less than 20 to stably form the oxide coating 15 having hydrogen radical resistance. Further, Sn/M in the absorption film 14 is more preferably within the range of 2 or more and 6 or less. When the content of the compound materials (metal element M other than Sn) in

the absorption film 14 is adjusted such that Sn/M is 2 or more and 6 or less, the oxide coating 15 can be more stably formed.

Further, the absorption film 14 may contain Sn in a proportion of 50 at% or more. Due to the fact that the absorption film 14 contains Sn in a proportion of 50 at% or more, the shadowing effect can be reduced and the transfer performance can be improved.

[0020]

Even when the absorption film 14 contains Sn in a proportion of 50 at% or more, the above-described compound materials containing the metal element M other than Sn, i.e., at least one of Cr, Ta, Nb, Ti, Al, V, and Hf, can be added to the absorption film 14. The mixing ratio of the compound materials (metal element M other than Sn) in the absorption film 14 containing Sn in a proportion of 50 at% or more needs to be larger than 5 at% and more preferably 15 at% or more with respect to the total atomic weight of the absorption film 14. When the absorption film 14 contains the compound materials in a proportion of more than 5 at%, the oxide coating 15 can be stably formed. When the absorption film 14 contains the compound materials in a proportion of 15 at% or more, the oxide coating 15 can be more stably formed.

As the metal element M other than Sn, Cr, Nb, and Hf among the elements mentioned above are more preferable because Cr, Nb, and Hf form a stable oxide coating.

[0021]

The absorption film 14 may contain at least one element selected from B, P, C, Si, and Ge as metalloid elements in addition to the elements mentioned above. By compounding these elements (metalloid elements) in the absorption film 14, the oxide coating 15 can be more stably formed. When the content of these elements is larger than the total atomic weight of the metal element M other than Sn, the formation of the oxide coating 15 becomes unstable, and therefore the content of these elements needs to be lower than the total atomic weight of the metal element M other than Sn. More specifically, with respect to a ratio of the total atomic weight of a metalloid element L to the total atomic weight of the metal element M other than Sn (hereinafter also simply referred to as "L/M"), L/M is desirably within the range of 0 or more and 1 or less and more preferably within the range of 0.1 or more and 0.5 or less to stably form the oxide coating 15. When L/M in the absorption film 14 is within the ranges above, the oxide coating 15 can be more stably formed.

[0022]

The absorption film 14 may not contain the metalloid elements mentioned above. In that case, L/M, which is the ratio of the total atomic weight of the metalloid element L to the total atomic weight of the metal element M other than Sn, is 0.

Among the elements mentioned above, B, P, and Si are more preferable as the metalloid elements, and P is the

most preferable because an oxide coating can be quickly formed.

[0023]

Further, the absorption film 14 contains, for
5 example, O or N as elements other than the metal element M other than Sn and the metalloid element L when Sn/M and L/M are within the numerical value ranges above.

[0024]

The absorption film 14 needs to be a material that
10 can be etched with a fluorine-based gas or a chlorine-based gas to form a fine pattern. Sn, Cr, Ta, Nb, Ti, Al, V, Hf, B, P, C, Si, and Ge, which are materials capable of constituting the absorption film 14, are materials that can be etched with a fluorine-based gas or
15 a chlorine-based gas and can finely form the absorption film pattern 14a.

[0025]

Herein, an optical density (OD) value, which is an index representing the contrast of the light intensities
20 of the multi-layer reflective film 12 and the absorption film 14, is described. When the intensity of a reflected light from the multi-layer reflective film 12 is defined as R_m and the intensity of a reflected light from the absorption film 14 is defined as R_a , the OD value is
25 defined by Expression (1) below.

$$OD = -\log(R_a/R_m) \quad \cdots \text{Equation (1)}$$

[0026]

When the OD value is larger, the contrast is better

and higher transferability is obtained. Although $OD > 1$ is required for the pattern transfer in the reflective photomask, the OD value of 1.5 or more is more preferable to obtain transfer performance higher than that of conventional films.

[0027]

The film thickness of the absorption film 14 (absorption film pattern 14a) is preferably 45 nm or less. When the film thickness of the absorption film 14 is 45 nm, the shadowing effect can be reduced and the transfer performance can be improved. The absorption film 14 preferably has a mixing ratio calculated such that the OD value is 1 or more to maintain a contrast that enables pattern transfer.

[0028] (Oxide coating)

The oxide coating 15 is a film resistant to hydrogen radicals and formed on the surface and the side surfaces of the absorption film pattern 14a. More specifically, the oxide coating 15 is a film formed to cover exposed parts of the absorption film pattern 14a.

The oxide coating 15 can be formed by forming the absorption film pattern 14a, and then oxidizing the surface of the absorption film pattern 14a, for example. Therefore, the absorption film 14 preferably contains a compound containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf. When the absorption film 14 contains the compound containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf, the compound containing at least one of Cr,

Ta, Nb, Ti, Al, V, and Hf can be easily added to the oxide coating 15.

[0029]

As described above, the oxide coating 15 preferably
5 contains a compound containing at least one of oxides of Cr, Ta, Nb, Ti, Al, V, and Hf. Among the elements described above, Cr, Nb, and Hf are more preferable because Cr, Nb, and Hf form a stable oxide coating.

The oxide coating 15 may not contain Sn. It may be
10 acceptable that the oxide coating 15 contains Sn, and the content of the Sn is smaller than the content of the compound containing at least one of oxides of Cr, Ta, Nb, Ti, Al, V, and Hf.

[0030]

15 Methods for forming the oxide coating 15 include methods in wet processes using chemical solutions represented by chemical treatment with chemical solutions, such as nitric acid or sulfuric acid, or electrochemical treatment, such as anode polarization in
20 chemical solutions, such as nitric acid or sulfuric acid, or in dry processes using an oxidizing gas, such as oxygen plasma. Chemical solutions or gases other than those mentioned above may be used to form the oxide coating 15, and several methods may be combined.

25 [0031]

Current EUV exposure devices are cleaned with hydrogen radicals to prevent the contamination inside a chamber due to contamination. Therefore, when reflective

photomasks have low durability to hydrogen radicals, the life of the masks is shortened. To prolong the life of the reflective photomasks, the reflective photomasks need to be formed of compound materials having high hydrogen radical resistance. Sn used as a material for the absorption film 14 has the high extinction coefficient k but has a problem that a simple Sn substance reacts with hydrogen radicals in the hydrogen radical environment and is converted to gaseous SnH_4 , which causes the film reduction of the absorption film pattern 14a.

[0032]

To use the reflective photomasks in the hydrogen radical environment, Sn may not be directly exposed to the hydrogen radicals. Specifically, when the oxide coating 15 formed of materials resistant to hydrogen radicals is present on the surface of the absorption film pattern 14a containing Sn, Sn is not exposed to the hydrogen radicals, which enables the long-term use thereof in the hydrogen radical environment, for example.

[0033]

The materials resistant to the hydrogen radicals are preferably compound materials exhibiting a film reduction of 1 nm or less in the hydrogen radical environment excited under a condition that the distance between electrodes 301 was set to 18 mm using a 2.45 GHz microwave plasma (MWP) at a hydrogen flow rate of 100 sscm using an apparatus illustrated in FIG. 3. In FIG. 3, a sample (test target) is denoted by "302" and a chamber is

denoted by "300".

[0034]

Materials forming the oxide coating 15 having hydrogen radical resistance include oxides of Cr, Ta, Nb, Ti, Al, V, and Hf. The oxide coating may contain elements inert to hydrogen radicals, such as F, as elements other than the metal elements mentioned above and O.

[0035]

10 The elements forming the oxide coating 15 are materials that are susceptible to oxidation, and therefore the surface of the absorption film 14 is sometimes naturally oxidized. These oxide films are very stable materials, and therefore the etching rate
15 deteriorates, which is disadvantageous for the formation of fine patterns in some cases. In that case, a hard mask layer for preventing the natural oxidation may be provided on the absorption film 14, for example.

Materials used for the hard mask layer are
20 preferably materials, such as SiO₂, SiON, TaO, TaN, TaBN, CrN, CrON, and CrO.

[0036]

The film thickness of the oxide coating 15 is preferably 1 nm or more and 10 nm or less. When the film
25 thickness of the oxide coating 15 is 1 nm or more, stable hydrogen radical resistance can be provided. When the film thickness of the oxide coating 15 is 10 nm or less, it is possible to reduce the shadowing effect or suppress

the influence on the optical properties, such as EUV reflectance and contrast, of the absorption film 14. The film thickness of the oxide coating 15 is more preferably 2 nm or more and 5 nm or less because the best balance
5 between the radical resistance and a change in the optical properties is achieved.

[0037]

The total film thickness of the absorption film 14 and the oxide coating 15 is more preferably 45 nm or
10 less. When the total film thickness of the absorption film 14 and the oxide coating 15 is 45 nm or less, the shadowing effect can be reduced and the transfer performance can be improved. To maintain the contrast that enables pattern transfer, the absorption film 14 and
15 the oxide coating 15 may be set to have an OD value of 1 or more as a whole.

[0038]

Herein, to evaluate the influence of the shadowing effect, it was compared by a simulation how an HV bias
20 value changes when each of absorption films was used, the absorption films each having a TiO₂ oxide coating (film thickness of 5 nm) formed on an existing Ta film (deposited film including a TaN layer for the lower layer and a TaO layer for the upper layer: film thickness of 60
25 nm) and on an Sn film containing Ti (film thickness of 40 nm). The HV bias value is a line width difference of a transfer pattern depending on the direction of a mask pattern, i.e., a difference between the line width in the

horizontal (H) direction and the line width in the vertical (V) direction. The line width in the H direction indicates the line width of a linear pattern orthogonal to a plane formed by an incident light and a reflected light (hereinafter sometimes referred to as "incident plane"). The line width in the V direction indicates the line width of a linear pattern parallel to the incident plane. More specifically, the line width in the H direction is the length in the direction parallel to the incident plane, and the line width in the V direction is the length in the direction orthogonal to the incident plane.

[0039]

The line width in the H direction is affected by the shadowing effect, which results in a decrease in the contrast at edge parts of the transfer pattern or a decrease in the line width in the H direction. The pattern affected by the shadowing effect has a line width after transfer smaller than a desired line width. On the other hand, the line width in the V direction is hardly affected by the shadowing effect. Therefore, a line width difference (HV bias) is generated between the line width of the transfer pattern in the direction perpendicular to the incident plane and the line width of the transfer pattern in the direction parallel to the incident plane.

[0040]

In the comparison of the HV bias values of the

absorption films each having the TiO₂ oxide coating formed on the existing Ta film and the Sn film containing Ti, a tantalum (Ta) mask of Reference Example and a reflective photomask of Example 1 in Table 1 were used.

5 When the HV bias values of the tantalum (Ta) mask of Reference Example and the reflective photomask of Example 1 were compared, the HV bias value of the Ta film is as extremely large as 7.3 nm, but the HV bias value of the absorption film having the TiO₂ coating formed on the Sn
10 film containing Ti can be greatly reduced to 5.7 nm, which is improved, as shown in Table 1. As described above, it is found in the reflective photomask 100 of this embodiment that the influence (HV bias) of the shadowing effect can be greatly reduced by the use of the
15 absorption film having the TiO₂ oxide coating 15 formed on the Sn film containing Ti for a formation material of the absorption film pattern 14a.

[0041] (Method for producing reflective photomask)

Next, a method for producing a reflective photomask
20 (reflective mask) is described using FIGS. 4 to 8.

As illustrated in FIG. 4, a positive chemically amplified resist (SEBP9012: manufactured by Shin-Etsu Chemical Co., Ltd.) was formed by spin coating to have a film thickness of 120 nm on the absorption film 14
25 provided on a reflective photomask blank 200, and then baked at 110°C for 10 min to form a resist film 17.

[0042]

Next, a predetermined pattern was drawn on the

resist film 17 formed of the positive chemically amplified resist by an electron beam lithography machine (JBX3030: manufactured by JEOL). Thereafter, baking treatment was performed at 110°C for 10 minutes, followed by spray development (SFG3000: manufactured by Sigma Meltec). This formed a resist pattern 17a as illustrated in FIG. 5.

[0043]

Next, as illustrated in FIG. 6, the absorption film 14 was patterned by dry etching mainly using a chlorine-based gas with the resist pattern 17a as an etching mask to form the absorption film pattern 14a.

[0044]

Next, the remaining resist pattern 17a was peeled off, thereby exposing the absorption film pattern 14a as illustrated in FIG. 7. In this embodiment, the absorption film pattern 14a formed in the absorption film 14 was set to an LS (line and space) pattern having a line width of 64 nm. The LS pattern having a line width of 64 nm was designed in each of the x-direction and the y-direction such that the influence of the shadowing effect by the EUV irradiation can be easily seen.

[0045]

Next, the surface of the absorption film pattern 14a was oxidized using a sulfuric acid solution having a weight concentration of 90% and a liquid temperature of 25°C to form the oxide coating 15 as illustrated in FIG. 8. At this time, the oxide coating 15 was formed on the

surface and the side surfaces of the absorption film 14 to cover the exposed parts of the absorption film pattern 14a. Thus, the reflective photomask 100 according to this embodiment is produced.

5 [0046] <Effects of this embodiment>

The reflective photomask 100 according to this embodiment has the following effects.

(1) In the reflective photomask 100 of this embodiment, the absorption film 14 (absorption film
10 pattern 14a) contains Sn and the metal element M other than Sn and has the ratio of the atomic weight of Sn to the total atomic weight of the metal element M other than Sn (Sn/Metal element M other than Sn) within the range of 1 or more and less than 20.

15 According to this configuration, the shadowing effect can be reduced and the transfer performance can be improved.

[0047]

(2) In the reflective photomask 100 of this
20 embodiment, the oxide coating 15 has hydrogen radical resistance and is formed on the surface and the side surfaces of the absorption film 14.

According to this configuration, the reflective photomask 100 has radical resistance, and thus the life
25 of the reflective photomask 100 can be prolonged.

[0048]

(3) In the reflective photomask 100 of this embodiment, the absorption film 14 may contain the

compound containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf. The absorption film 14 may contain the compound containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf in an amount larger than 5 at% of the total
5 atomic weight of the absorption film 14.

According to this configuration, the oxide coating 15 having hydrogen radical resistance can be stably formed.

[0049]

10 (4) In the reflective photomask 100 of this embodiment, the absorption film 14 may contain at least one of B, C, P, Si, and Ge as the metalloid element L. As the content of the metalloid element L, L/M may be within the range of 0 or more and 1 or less with respect
15 to the total atomic weight of the metal element M other than Sn. It is a matter of course that, in the reflective photomask 100 of this embodiment, the absorption film 14 may not contain at least one of B, C, P, Si, and Ge as the metalloid element L.

20 According to this configuration, the oxide coating 15 having hydrogen radical resistance can be more stably formed.

[0050]

(5) In the reflective photomask 100 of this
25 embodiment, the absorption film 14 may be able to be etched with a fluorine-based gas or a chlorine-based gas.

According to this configuration, a fine pattern can be formed in the absorption film 14.

(6) In the reflective photomask 100 of this embodiment, the OD value may be 1.0 or more.

According to this configuration, the absorption film 14 can maintain the contrast that enables pattern transfer.

[0051]

(7) In the reflective photomask 100 of this embodiment, the absorption film 14 may contain Sn in a proportion of 50 at% or more.

According to this configuration, the shadowing effect can be reduced and the transfer performance can be improved.

(8) In the reflective photomask 100 of this embodiment, the oxide coating 15 may contain the compound containing at least one of oxides of Cr, Ta, Nb, Ti, Al, V, and Hf.

According to this configuration, the oxide coating 15 having hydrogen radical resistance can be stably formed.

[0052]

(9) In the reflective photomask 100 of this embodiment, the oxide coating 15 may not contain Sn. It may be acceptable that the oxide coating 15 contains Sn, and the content of Sn may be smaller than the content of the compound containing at least one of oxides of Cr, Ta, Nb, Ti, Al, V, and Hf.

According to this configuration, the oxide coating 15 having hydrogen radical resistance can be stably

formed.

[0053]

(10) In the reflective photomask 100 of this embodiment, the oxide coating 15 may have a film
5 thickness of 1 nm or more.

According to this configuration, the oxide coating 15 having hydrogen radical resistance can be stably formed.

[0054]

10 (11) In the reflective photomask 100 of this embodiment, the total film thickness of the absorption film 14 and the oxide coating 15 may be 45 nm or less.

According to this configuration, the shadowing effect can be reduced and the transfer performance can be
15 improved.

Examples

[0055]

Hereinafter, the present disclosure is described in
20 more detail with respect to Examples but the present disclosure is not limited by Examples at all.

<Example 1>

A synthetic quartz substrate having low thermal expansion characteristics was used as a substrate. On
25 the substrate, a multi-layer reflective film was formed by depositing 40 multi-layer films each containing a pair of silicon (Si) and molybdenum (Mo). The film thickness of the multi-layer reflective film was set to 280 nm.

Next, a protective film was formed using ruthenium (Ru) such that the film thickness was 2.5 nm on the multi-layer reflective film.

[0056]

5 On the protective film, an absorption film was formed using tin (Sn) and titanium (Ti). At this time, the absorption film was formed such that the total film thickness with an oxide coating described later was 45 nm. The atomic number ratio of tin (Sn) and titanium
10 (Ti) was 80.0:20.0 as measured by XPS (X-ray photoelectron spectroscopy). Therefore, it was found that Sn/M was 4 and L/M was 0. The measurement by an XRD (X-ray diffraction device) showed that the absorption
15 film was amorphous although crystallinity was slightly observed.

Next, on the side where the multi-layer reflective film was not formed of the substrate, a back surface conductive film was formed using chromium nitride (CrN) such that the thickness was 100 nm.

20 [0057]

For the formation of each film on the substrate, a multi-source sputtering apparatus was used. The film thickness of each film was controlled by a sputtering time.

25 [0058]

Next, a positive chemically amplified resist (SEBP9012: manufactured by Shin-Etsu Chemical Co., Ltd.) was formed by spin coating to have a film thickness of

120 nm on the absorption film, and then baked at 110°C for 10 min to form a resist film.

Next, a predetermined pattern was drawn on the positive chemically amplified resist by an electron beam lithography machine (JBX3030: manufactured by JEOL).

Thereafter, baking treatment was performed at 110°C for 10 minutes, followed by spray development (SFG3000: manufactured by Sigma Meltec). This formed a resist pattern.

10 [0059]

Next, the absorption film was patterned by dry etching mainly using a chlorine-based gas with the resist pattern as an etching mask to form an absorption film pattern.

15 Next, the remaining resist pattern was peeled off. Thus, an absorption film pattern was formed in which the surface and the side surfaces of the absorption film were exposed.

[0060]

20 In this example, the absorption film pattern was set to an LS (line and space) pattern having a line width of 64 nm. The LS pattern having a line width of 64 nm was designed in each of the x-direction and the y-direction such that the influence of the shadowing effect by the EUV irradiation can be easily seen.

25 [0061]

Next, an oxide coating was formed using a sulfuric acid solution having a weight concentration of 90% and a

liquid temperature of 25°C. When the film thickness and the composition were confirmed with a transmission electron microscope (TEM), it was found that the oxide coating was formed such that the film thickness was 5 nm and the composition was Ti:O = 1:2 and that the total film thickness of the oxide coating and the absorption film was 45 nm. As described above, a reflective photomask of Example 1 was produced.

[0062]

10 The absorption film of Example 1 was measured for a reflectance R_m of a multi-layer reflective film region and a reflectance R_a of an absorption film region with a reflectance measuring device using the EUV light. From the measurement results, the OD value, which is the mask characteristic, was calculated. As a result, it was found that the reflective photomask was produced such that the EUV reflectance was 0.72% and the OD value was 1.9 as shown in Table 1.

[0063] <Example 2>

20 The absorption film was formed by changing the material of the absorption film to tin (Sn) and chromium (Cr). At this time, the atomic number ratio of tin (Sn) and chromium (Cr) was set to 80.0:20.0. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, 25 the composition of the oxide coating was Cr:O = 2:3. A reflective photomask of Example 2 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 2 had the EUV

reflectance of 0.50% and the OD value of 2.1.

[0064] <Example 3>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and niobium (Nb). At this time, the atomic number ratio of tin (Sn) and niobium (Nb) was set to 80.0:20.0. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was Nb:O = 2:3. A reflective photomask of Example 3 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 3 had the EUV reflectance of 0.34% and the OD value of 2.3.

[0065] <Example 4>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and tantalum (Ta). At this time, the atomic number ratio of tin (Sn) and tantalum (Ta) was set to 80.0:20.0. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was Ta:O = 2:5. A reflective photomask of Example 4 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 4 had the EUV reflectance of 0.34% and the OD value of 2.3.

[0066] <Example 5>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and aluminum (Al). At this time, the atomic number ratio of tin (Sn) and aluminum (Al) was set to 80.0:20.0. Therefore, it

was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was Al:O = 2:3. A reflective photomask of Example 5 was produced in the same manner as in Example 1 except for the above.

5 The reflective photomask of Example 5 had the EUV reflectance of 0.25% and the OD value of 2.4.

[0067] <Example 6>

 The absorption film was formed by changing the material of the absorption film to tin (Sn) and vanadium
10 (V). At this time, the atomic number ratio of tin (Sn) and vanadium (V) was set to 80.0:20.0. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was V:O = 2:5. A reflective photomask of Example 6 was produced in the
15 same manner as in Example 1 except for the above.

 The reflective photomask of Example 6 had the EUV reflectance of 0.39% and the OD value of 2.2.

[0068] <Example 7>

 The absorption film was formed by changing the
20 material of the absorption film to tin (Sn) and hafnium (Hf). At this time, the atomic number ratio of tin (Sn) and hafnium (Hf) was set to 80.0:20.0. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was Hf:O = 1:2. A
25 reflective photomask of Example 7 was produced in the same manner as in Example 1 except for the above.

 The reflective photomask of Example 7 had the EUV reflectance of 0.44% and the OD value of 2.2.

[0069] <Example 8>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and hafnium (Hf). At this time, the atomic number ratio of tin (Sn) and hafnium (Hf) was set to 95.0:5.0. Therefore, it was found that Sn/M was 19 and L/M was 0. Consequently, the composition of the oxide coating was Hf:Sn:O = 1:1:2 and an oxide coating containing only HfO₂ was not formed. A reflective photomask of Example 8 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 8 had the EUV reflectance of 0.25% and the OD value of 2.4.

[0070] <Example 9>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and titanium (Ti). At this time, the atomic number ratio of tin (Sn) and titanium (Ti) was set to 93.8:6.2. Therefore, it was found that Sn/M was 15 and L/M was 0. Consequently, the composition of the oxide coating was Ti:Sn:O = 1:1:2 and an oxide coating containing only TiO₂ was not formed. A reflective photomask of Example 9 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 9 had the EUV reflectance of 0.36% and the OD value of 2.3.

[0071] <Example 10>

The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), and boron (B). At this time, the atomic number

ratio of tin (Sn), titanium (Ti), and boron (B) was set to 90.9:6.1:3.0. Therefore, it was found that Sn/M was 15 and L/M was 0.5. Consequently, the composition of the oxide coating was Ti:O = 1:2. A reflective photomask of Example 10 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 10 had the EUV reflectance of 0.42% and the OD value of 2.2.

[0072] <Example 11>

10 The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), and carbon (C). At this time, the atomic number ratio of tin (Sn), titanium (Ti), and carbon (C) was set to 90.9:6.1:3.0. Therefore, it was found that Sn/M was 15 and L/M was 0.5. Consequently, the composition of the oxide coating was Ti:O = 1:2. A reflective photomask of Example 11 was produced in the same manner as in Example 1 except for the above.

20 The reflective photomask of Example 11 had the EUV reflectance of 0.42% and the OD value of 2.2.

[0073] <Example 12>

25 The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), and phosphorus (P). At this time, the atomic number ratio of tin (Sn), titanium (Ti), and phosphorus (P) was set to 90.9:6.1:3.0. Therefore, it was found that Sn/M was 15 and L/M was 0.5. Consequently, the composition of the oxide coating was Ti:O = 1:2. A

reflective photomask of Example 12 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 12 had the EUV reflectance of 0.43% and the OD value of 2.2.

5 [0074] <Example 13>

The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), and silicon (Si). At this time, the atomic number ratio of tin (Sn), titanium (Ti), and silicon (Si) was
10 set to 90.9:6.1:3.0. Therefore, it was found that Sn/M was 15 and L/M was 0.5. Consequently, the composition of the oxide coating was Ti:O = 1:2. A reflective photomask of Example 13 was produced in the same manner as in Example 1 except for the above.

15 The reflective photomask of Example 13 had the EUV reflectance of 0.43% and the OD value of 2.2.

[0075] <Example 14>

The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium
20 (Ti), and oxygen (O). At this time, the atomic number ratio of tin (Sn), titanium (Ti), and oxygen (O) was set to 27.4:6.8:65.8. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was Ti:O = 1:2. A reflective photomask of
25 Example 14 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 14 had the EUV reflectance of 0.60% and the OD value of 2.0.

[0076] <Example 15>

The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), boron (B), and oxygen (O). At this time, the atomic number ratio of tin (Sn), titanium (Ti), boron (B), and oxygen (O) was set to 28.8:4.8:1.0:65.4. Therefore, it was found that Sn/M was 6 and L/M was 0.2. Consequently, the composition of the oxide coating was Ti:O = 1:2. A reflective photomask of Example 15 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 15 had the EUV reflectance of 0.54% and the OD value of 2.1.

[0077] <Example 16>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and bismuth (Bi). At this time, the atomic number ratio of tin (Sn) and bismuth (Bi) was set to 80.0:20.0. Therefore, it was found that Sn/M was 4 and L/M was 0. Consequently, the composition of the oxide coating was Bi:O = 2:3. A reflective photomask of Example 16 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 16 had the EUV reflectance of 0.19% and the OD value of 2.5.

[0078] <Example 17>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and titanium (Ti). At this time, the atomic number ratio of tin (Sn)

and titanium (Ti) was set to 93.8:6.2. Therefore, it was found that Sn/M was 15 and L/M was 0. Further, the oxide coating was formed using a sulfuric acid solution having a weight concentration of 60% and a liquid temperature of 25°C. Consequently, the composition of the oxide coating was Ti:Sn:O = 1:2:4 and an oxide coating containing only TiO₂ was not formed. A reflective photomask of Example 17 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 17 had the EUV reflectance of 0.36% and the OD value of 2.3.

[0079] <Example 18>

The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), and boron (B). At this time, the atomic number ratio of tin (Sn), titanium (Ti), and boron (B) was set to 86.7:5.8:7.5. Therefore, it was found that Sn/M was 15 and L/M was 1.3. Consequently, the film thickness of the oxide coating was 2 nm and the composition of the oxide coating was Ti:Sn:O = 1:1:2. A reflective photomask of Example 18 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Example 18 had the EUV reflectance of 0.27% and the OD value of 2.4

[0080] <Comparative Example 1>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and titanium (Ti). At this time, the atomic number ratio of tin (Sn)

and titanium (Ti) was set to 30.0:70.0. Therefore, it was found that Sn/M was 0.4 and L/M was 0. Consequently, the composition of the oxide coating was Ti:O = 1:2. A reflective photomask of Comparative Example 1 was
5 produced in the same manner as in Example 1 except for the above.

The reflective photomask of Comparative Example 1 had the EUV reflectance of 5.40% and the OD value of 1.1.
[0081] <Comparative Example 2>

10 The absorption film was formed by changing the material of the absorption film to tin (Sn), titanium (Ti), and boron (B). At this time, the atomic number ratio of tin (Sn), titanium (Ti), and boron (B) was set to 66.7:11.1:22.2. Therefore, it was found that Sn/M was
15 6 and L/M was 2. An oxide coating containing titanium oxide was not formed. A reflective photomask of Comparative Example 2 was produced in the same manner as in Example 1 except for the above.

The reflective photomask of Comparative Example 2
20 had the EUV reflectance of 0.58% and the OD value of 2.0.
[0082] <Comparative Example 3>

The absorption film was formed by changing the material of the absorption film to tin (Sn) and titanium (Ti). At this time, the atomic number ratio of tin (Sn)
25 and titanium (Ti) was set to 95.2:4.8. Therefore, it was found that Sn/M was 20 and L/M was 0. An oxide coating containing titanium oxide was not formed. A reflective photomask of Comparative Example 3 was produced in the

same manner as in Example 1 except for the above.

The reflective photomask of Comparative Example 3 had the EUV reflectance of 0.02% and the OD value of 3.5.

[0083] <Evaluation>

5 The reflective photomasks obtained in Examples 1 to 18 and Comparative Examples 1 to 3 above were evaluated for the transfer performance and the hydrogen radical resistance by the following methods. The transfer performance was confirmed by wafer exposure evaluation.

10 The above-described "existing tantalum (Ta) mask" is indicated as "Reference Example" in Table 1.

[0084] [Wafer exposure evaluation]

 The absorption film pattern of the reflective photomask produced in each of Examples and Comparative
15 Examples was transferred and exposed onto a semiconductor wafer coated with an EUV positive chemically amplified resist using an EUV exposure device (NXE3300B: manufactured by ASML). At this time, the exposure amount was adjusted such that the LS pattern in the x-direction
20 was transferred as designed. Thereafter, the observation and the line width measurement of the transferred resist pattern were carried out with an electron beam dimension measuring machine, and the resolution and the HV bias were confirmed from the measurement results.

25 [0085] <Evaluation criteria>

 The evaluation was performed based on the size (Large or Small) of the HV bias in comparison with a case where the existing tantalum (Ta) mask was used. More

specifically, a case where the LS pattern in the y-direction was transferred as designed in a state where the adjustment was performed such that the LS pattern in the x-direction was transferred as designed and the HV bias was smaller than that when the existing tantalum (Ta) mask was used was evaluated as "Pass". A case where the LS pattern in the y-direction was not transferred as designed (LS pattern in the y-direction was not resolved) in a state where the adjustment was performed such that the LS pattern in the x-direction was transferred as designed or a case where the HV bias is larger than that when the existing tantalum (Ta) mask was used was evaluated as "Failure"

[0086] [Hydrogen radical resistance]

Hydrogen at a flow rate of 100 sscm was excited using a 2.45 GHz micro wave plasma (MWP), and the produced reflective photomask was placed on one of electrodes with an inter-electrode distance of 18 mm. A change in the film thickness of the absorption film after the hydrogen radical treatment was confirmed using an atomic force microscopy (AFM) and was evaluated in the following three grades of ◎, ○, and ×. The measurement was performed with a LS pattern having a line width of 200 nm.

<Evaluation criteria>

◎: No change in film thickness to hydrogen radicals was observed.

○: A slight change in film thickness to hydrogen

radicals was observed.

×: A change in film thickness to hydrogen radicals was observed.

[0087]

5 Further, in the column of "Mask characteristic" in Table 1, the evaluation was performed in the following three grades of ◎, Δ, and × from the viewpoint of the OD value and the transferability compared with those of the existing tantalum (Ta) mask.

10 <Evaluation criteria>

◎: Superiority was found in terms of both the OD value and the transferability.

Δ: Superiority was not found in terms of either the OD value or the transferability.

15 ×: Both the OD value and the transferability were inferior.

[0088]

In the column of "Determination" in Table 1, the evaluation was performed in the following four grades of
20 ◎, ○, Δ, and ×.

<Evaluation criteria>

◎: Both the mask characteristic and the hydrogen radical resistance were evaluated as ◎.

○: The mask characteristic was evaluated as ◎ and
25 the hydrogen radical resistance was evaluated as ○.

Δ: The mask characteristic was evaluated as Δ and the hydrogen radical resistance was evaluated as ◎ or ○.

×: Either or both the mask characteristic or/and the

hydrogen radical resistance was/were evaluated as ×.

The evaluation results above are shown in Table 1.

[0089]

[Table 1]

	Absorption film		Oxide coating		Total film thickness (nm) of absorption film and oxide coating	Optical characteristics		Evaluation					Determination
	Materials (Sn/M, L/M)	Film thickness (nm)	Material	Film thickness (nm)		Reflectance (%)	OD value	x-direction dimension (nm)	y-direction dimension (nm)	HV bias (nm)	Mack characteristic	Hydrogen radical resistance	
Ex. 1	Sn + Ti (4, 0)	40	TiO ₂	5	45	0.72	1.9	16.0	10.3	5.7	◎	◎	◎
Ex. 2	Sn + Cr (4, 0)	40	Cr ₂ O ₃	5	45	0.50	2.1	16.0	9.8	6.2	◎	◎	◎
Ex. 3	Sn + Nb (4, 0)	40	Na ₂ O ₃	5	45	0.34	2.3	16.0	10.7	5.3	◎	◎	◎
Ex. 4	Sn + Ta (4, 0)	40	Ta ₂ O ₅	5	45	0.34	2.3	16.0	10.4	5.6	◎	◎	◎
Ex. 5	Sn + Al (4, 0)	40	Al ₂ O ₃	5	45	0.25	2.4	16.0	10.9	5.1	◎	◎	◎
Ex. 6	Sn + V (4, 0)	40	V ₂ O ₅	5	45	0.39	2.2	16.0	10.5	5.5	◎	◎	◎
Ex. 7	Sn + Hf (4, 0)	40	HfO ₂	5	45	0.44	2.2	16.0	10.2	5.8	◎	◎	◎
Ex. 8	Sn + Hf (19, 0)	40	Hf + Sn + O	5	45	0.25	2.4	16.0	10.2	5.8	◎	○	○
Ex. 9	Sn + Ti (15, 0)	40	Ti + Sn + O	5	45	0.36	2.3	16.0	10.1	5.9	◎	○	○
Ex. 10	Sn + Ti + B (15, 0.5)	40	TiO ₂	5	45	0.42	2.2	16.0	10.1	5.9	◎	◎	◎
Ex. 11	Sn + Ti + C (15, 0.5)	40	TiO ₂	5	45	0.42	2.2	16.0	10.0	6.0	◎	◎	◎
Ex. 12	Sn + Ti + P (15, 0.5)	40	TiO ₂	5	45	0.43	2.2	16.0	10.1	5.9	◎	◎	◎
Ex. 13	Sn + Ti + Si (15, 0.5)	40	TiO ₂	5	45	0.43	2.2	16.0	10.1	5.9	◎	◎	◎
Ex. 14	Sn + Ti + O (4, 0)	40	TiO ₂	5	45	0.60	2.0	16.0	10.1	5.9	◎	◎	◎
Ex. 15	Sn + Ti + B + O (6, 0.2)	40	TiO ₂	5	45	0.54	2.1	16.0	10.1	5.9	◎	◎	◎
Ex. 16	Sn + Bi (4, 0)	40	Bi ₂ O ₃	5	45	0.19	2.5	16.0	9.3	6.7	◎	○	○
Ex. 17	Sn + Ti (15, 0)	40	Ti + Sn + O (Sn > Ti)	5	45	0.36	2.3	16.0	10.1	5.9	◎	○	○
Ex. 18	Sn + Ti + B (15, 1.3)	40	Ti + Sn + O	2	42	0.27	2.4	16.0	9.9	6.1	◎	○	○
Comp. Ex. 1	Sn + Ti (0.4, 0)	40	TiO ₂	5	45	5.40	1.1	16.0	11.5	4.5	△	◎	△
Comp. Ex. 2	Sn + Ti + B (6, 2)	40	-	-	40	0.58	2.0	16.0	11.0	5.0	◎	×	×
Comp. Ex. 3	Sn + Ti (20, 0)	40	-	-	40	0.02	3.5	16.0	10.5	5.5	◎	×	×
Ref. Ex.	TaO (Upper layer) 2 nm Ta ₂ N (Lower layer) 58 nm	60	-	-	60	1.83	1.5	16.0	8.7	7.3	△	◎	△

[0090]

As shown in Table 1, it was found from the evaluation results of Examples 1 to 18 and Comparative Examples 1 to 3 that, when the absorption film has Sn/M of 1 or more as in Examples 1 to 18, the reflectance is lower than that when the absorption film has Sn/M of less than 1 as in Comparative Example 1, and the shadowing effect can be reduced.

[0091]

It was also found from the evaluation results of Examples 1 to 9, 16, 18 and Comparative Example 3 that, when Sn/M is less than 20 as in Examples 1 to 9, 16, 18, the hydrogen radical resistance is higher than that when Sn/M is 20 or more as in Comparative Example 3.

[0092]

Further, it was found from the evaluation results of Example 9 and Examples 10 to 13, 17 that, when the metalloid elements are contained, the hydrogen radical resistance is improved by stably forming the oxide coating even when Sn/M is large.

It was also found that the hydrogen radical resistance in Examples 10 to 13 is higher than that when L/M is larger than 1 as in Comparative Example 2.

[0093]

It was also found from the evaluation results of Examples 14 and 15 that, even when the element other than Sn and the metal elements and the metalloid elements mentioned above, such as oxygen, is contained, the

hydrogen radical resistance is high when the oxide coating is formed.

[0094]

The reflective mask and the method for producing a
5 reflective mask of the present disclosure are not limited to the embodiment and Examples described above and can be variously modified without impairing the features of the invention.

10 Reference Signs List

[0095]

- 11: substrate
- 12: multi-layer reflective film
- 13: protective film
- 15 14: absorption film
- 14a: absorption film pattern
- 15: oxide coating
- 16: back surface conductive film
- 17: resist film
- 20 100: reflective photomask (reflective mask)
- 200: reflective photomask blank (reflective mask blank)
- 300: chamber
- 301: electrode
- 25 302: sample

CLAIMS

1. A reflective mask comprising:

a substrate;

5 a reflective film configured to reflect an EUV light having a multi-layer film structure formed on the substrate;

a protective film formed on the reflective film, and configured to protect the reflective film;

10 an absorption film configured to absorb the EUV light formed on the protective film; and

an oxide coating formed on the absorption film; wherein

the absorption film contains Sn and a metal element
15 other than Sn and has a ratio of an atomic weight of the Sn to a total atomic weight of the metal element other than Sn (Sn/Metal element other than Sn) within a range of 1 or more and less than 20, and

the oxide coating is resistant to a hydrogen radical
20 and formed on a surface and side surfaces of the absorption film.

2. A reflective mask comprising:

a substrate;

25 a reflective film configured to reflect an EUV light having a multi-layer film structure formed on the substrate;

a protective film formed on the reflective film, and

configured to protect the reflective film;

an absorption film configured to absorb the EUV light formed on the protective film; and

an oxide coating formed on the absorption film;

5 wherein

the absorption film contains Sn in a proportion of 50 at% or more, and

the oxide coating is resistant to a hydrogen radical and formed on a surface and side surfaces of the
10 absorption film.

3. The reflective mask according to claim 1 or 2, wherein the oxide coating contains a compound containing at least one of oxides of Cr, Ta, Nb, Ti, Al,
15 V, and Hf.

4. The reflective mask according to any one of claims 1 to 3, wherein the oxide coating does not contain Sn or the oxide coating contains Sn, and a content of the
20 Sn is smaller than a content of the compound containing at least one of oxides of Cr, Ta, Nb, Ti, Al, V, and Hf.

5. The reflective mask according to any one of claims 1 to 4, wherein the absorption film contains a
25 compound containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf as the metal element other than Sn.

6. The reflective mask according to any one of

claims 1 to 5, wherein the oxide coating has a film thickness of 1 nm or more.

7. The reflective mask according to any one of
5 claims 1 to 6, wherein the absorption film does not contain B, C, P, Si, and Ge, which are metalloid elements, or contains at least one of the metalloid elements, and has a ratio of a total atomic weight of the
10 metalloid element to a total atomic weight of the metal element other than Sn (Metalloid element/Metal element other than Sn) within a range of 0 or more and 1 or less.

8. The reflective mask according to any one of
15 claims 1 to 7, wherein the absorption film contains the compound containing at least one of Cr, Ta, Nb, Ti, Al, V, and Hf in a proportion of more than 5 at%.

9. The reflective mask according to any one of
20 claims 1 to 8, wherein the absorption film is able to be etched with a fluorine-based gas or a chlorine-based gas.

10. The reflective mask according to any one of
claims 1 to 9, wherein a total film thickness of the absorption film and the oxide coating is 45 nm or less,
25 and an OD value (Optical Density) is 1.0 or more.

11. A method for producing a reflective mask, the reflective mask including:

a substrate;
a reflective film configured to reflect an EUV light
having a multi-layer film structure formed on the
substrate;
5 a protective film configured to protect the
reflective film formed on the reflective film;
an absorption film configured to absorb the EUV
light formed on the protective film; and
an oxide coating formed on the absorption film;
10 wherein
the absorption film contains Sn and a metal element
other than Sn and has a ratio of an atomic weight of the
Sn to a total atomic weight of the metal element other
than Sn (Sn/Metal element other than Sn) within a range
15 of 1 or more and less than 20, and
the oxide coating is resistant to a hydrogen radical
and formed on a surface and side surfaces of the
absorption film.

20 12. A method for producing a reflective mask, the
reflective mask including:

a substrate;
a reflective film configured to reflect an EUV light
having a multi-layer film structure formed on the
25 substrate;
a protective film configured to protect the
reflective film formed on the reflective film;
an absorption film configured to absorb the EUV

light formed on the protective film; and

an oxide coating formed on the absorption film;

wherein

the absorption film contains Sn in a proportion of

5 50 at% or more, and

the oxide coating is resistant to a hydrogen radical
and formed on a surface and side surfaces of the
absorption film.

10 13. The method for producing a reflective mask
according to claim 11 or 12, wherein the oxide coating is
formed by oxidizing the absorption film.