

SUBSTRATE TREATMENT METHOD AND SUBSTRATE TREATMENT DEVICE

TECHNICAL FIELD

[0001] Various aspects and embodiments of the present disclosure relate to a substrate processing method and a substrate processing apparatus.

BACKGROUND

[0002] Patent Document 1 discloses a method for manufacturing a high-silicon steel strip in a continuous line, wherein a steel strip is continuously siliconized at a temperature of 1,023 to 1,200 degrees C by chemical vapor deposition in a non-oxidizing gas atmosphere containing 5 to 35 mol% of SiCl_4 , followed by a diffusion process in a non-oxidizing gas atmosphere without containing SiCl_4 to substantially uniformly diffuse Si into the steel strip, and then wound after cooling.

[Prior Art Document]

[Patent Document]

[0003] Patent Document 1: Japanese Patent Laid-open Publication No. S62-227078

SUMMARY

[0004] The present disclosure provides a substrate processing method and a substrate processing apparatus, which are capable of improving processability of a photoresist film in EUV exposure.

[0005] A substrate processing method according to one embodiment of the present disclosure includes a) and b). In a), a substrate having a surface on which a photoresist film containing a metal oxide is formed is placed in a chamber. In b), a silicon-containing gas is supplied into the chamber to substitute a metal, which constitutes the metal oxide contained in the photoresist film, with silicon.

[0006] According to the present disclosure, it is possible to improve processability of a photoresist film in EUV exposure.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. 1 is a diagram illustrating atomic EUV absorption cross sections.

FIG. 2 is a diagram for explaining an example of a substrate according to an embodiment.

FIG. 3 is a diagram for explaining an example of a flow of substrate processing for forming a pattern on a substrate.

FIGS. 4A and 4B are diagrams illustrating examples of a substitution state in a metal oxide resist film of a substrate according to an embodiment.

FIG. 5 is a diagram illustrating an example of a schematic configuration of a substrate processing apparatus according to an embodiment.

FIG. 6 is a flowchart illustrating an example of substrate processing according to an embodiment.

FIG. 7 is a diagram for explaining an example of a flow of substrate processing for performing double patterning on a substrate.

DETAILED DESCRIPTION

[0008] Hereinafter, embodiments of a substrate processing method and a substrate processing apparatus disclosed herein will be described in detail with reference to the drawings. However, the substrate processing method and the substrate processing apparatus disclosed herein are not limited to the embodiments to be described below.

[0009] In manufacturing semiconductor devices, patterns are formed on a substrate such as a semiconductor wafer by a lithography process. In the lithography process, a photoresist film is formed on a surface of the substrate. Further, in the lithography process, selective exposure is performed on the formed photoresist film through a mask formed with a predetermined pattern, followed by development to form a pattern of a predetermined shape in the photoresist film. Conventionally, carbon-based photoresists have been used. For example, chemically amplified resists have been widely used.

[0010] In recent years, with miniaturization of semiconductor devices, miniaturization has also

progressed in lithography technology. One approach to the miniaturization is shortening a wavelength of an exposure light source. Recently, extreme ultra violet (EUV) exposure using EUV light is being studied.

[0011] However, the conventional carbon-based photoresist films absorb EUV poorly and require longer reaction times. Therefore, in EUV exposure, photoresist films containing metal oxides are used. For example, in EUV exposure, metal oxide resists (MOR), such as tin oxide, are used for photoresist films.

[0012] FIG. 1 is a diagram illustrating atomic EUV absorption cross sections. In FIG. 1, a horizontal axis represents an atomic number of each atom, and a vertical axis represents an atomic absorption cross section. The absorption cross section indicates a proportion of EUV absorbed when passing through atoms. The atomic absorption cross section corresponding to each atomic number is shown in FIG. 1. For example, the absorption cross section of atomic number 12 is an absorption cross section of carbon, and the absorption cross section of atomic number 50 is an absorption cross section of tin. Tin has a larger EUV absorption cross section than carbon. That is, tin has a higher EUV absorption rate than carbon.

[0013] However, the metal oxide resists have poorer processability than the conventional carbon-based photoresists. Therefore, the present disclosure provides a technique for improving processability of a photoresist film in EUV exposure.

(Embodiments)

[0014] Embodiments will now be described. First, an example of a substrate 10 for use in substrate processing according to an embodiment will be described. FIG. 2 is a diagram for explaining an example of the substrate 10 according to the embodiment. The substrate 10 is illustrated in FIG. 2. The substrate 10 includes a first underlying film 12 and a second underlying film 13 sequentially stacked on a silicon substrate 11. The first underlying film 12 may be, for example, any of SiC(H), SiOC(H), SiOCN, SiO_x, SiN_x, and spin on glass (SOG). The second underlying film 13 may be, for example, any of SiC(H), SiOC(H), SiOCN, SiO_x, SiN_x, diamond-like carbon (DLC), amorphous carbon (a-C), and SOG. A configuration of the

substrate 10 illustrated in FIG. 2 is an example, and the substrate 10 is not limited thereto.

Films required for manufacturing a semiconductor device may be formed on the substrate 10 as necessary.

[0015] In manufacturing a semiconductor device, a pattern is formed on the substrate 10 by a lithography process. In the lithography process, a photoresist film containing a metal oxide is formed on a surface of the substrate 10. The metal oxide is an oxide of any of Sn (tin), W (tungsten), Te (tellurium), Sb (antimony), In (indium), Zn (zinc), Zr (zirconium), and Hf (hafnium). For example, in EUV exposure, a metal oxide resist film 20 is formed on the surface of the substrate 10 as a photoresist film. For example, a tin oxide film is formed on the substrate 10 as the metal oxide resist film 20.

[0016] Next, an example of a flow of substrate processing for forming a pattern on the substrate 10 according to an embodiment will be described. FIG. 3 is a diagram for explaining an example of a flow of substrate processing for forming a pattern on the substrate 10. The metal oxide resist film 20 has been formed on the surface of the substrate 10.

[0017] When forming a pattern on the metal oxide resist film 20 of the substrate 10, EUV exposure is performed. In the EUV exposure, EUV light is irradiated onto the metal oxide resist film 20 of the substrate 10 via a mask 30 formed with a predetermined pattern. In the metal oxide resist film 20, an exposed portion 20a irradiated by the EUV light and an unexposed portion 20b without being irradiated by the EUV light are formed correspondingly to the mask 30. Subsequently, post-exposure bake (PEB) is performed. In the post-exposure bake, the substrate 10 subjected to the EUV exposure is heated to promote a reaction in the exposed portion 20a of the metal oxide resist film 20. Thereafter, development of the substrate 10 is performed. For example, the metal oxide resist film 20 has a difference in etch rate between the exposed portion 20a and the unexposed portion 20b. By etching the metal oxide resist film 20 by using a selectivity between the exposed portion 20a and the unexposed portion 20b, the substrate 10 is developed. For example, when the metal oxide resist film 20 is a tin oxide (SnO_x) film, the exposed portion 20a of the metal oxide resist film 20 is converted into SnO_2 by the EUV exposure. Since SnO_2 in the exposed portion 20a and SnO_x in the unexposed portion

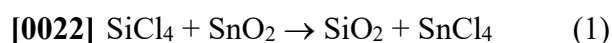
20b can provide an etch selectivity therebetween, it is possible to perform a negative-tone patterning that removes the unexposed portion 20b by etching while leaving the exposed portion 20a. FIG. 3 shows a case in which negative-tone development is performed to leave the exposed portion 20a of the metal oxide resist film 20.

[0018] However, the metal oxide resist film 20 has poorer processability than a carbon-based resist. For example, the metal oxide resist film 20 is prone to generating residues, which are difficult to remove. For example, residues of SnO may remain on the metal oxide resist film 20. When the residues remain on the metal oxide resist film 20, the residues may be transferred during transfer of a pattern to the substrate 10, resulting in deterioration of pattern fidelity and degradation of surface roughness. Further, etching of SnO requires gases that are difficult to handle, such as HBr or BCl₃.

[0019] Therefore, in the substrate processing according to the embodiment, the substrate 10 is exposed to a silicon-containing gas. For example, the substrate 10 is placed inside a chamber. Thereafter, a silicon-containing gas is supplied into the chamber, and the substrate 10 is exposed to the silicon-containing gas. The silicon-containing gas includes a silicon halide and a hydride. The silicon halide and the hydride may form a silicon oxide and selected from the group consisting of SiCl₄ (tetrachlorosilane), SiH₂Cl₂ (dichlorosilane), SiF₄ (tetrafluorosilane), SiH₄ (monosilane), Si₂H₆ (disilane), and Si₂Cl₆ (hexachlorodisilane). Examples of the silicon halide include SiH₂Cl₂, Si₂Cl₆, SiCl₄, and SiF₄. Examples of the hydride include SiH₄ and Si₂H₆. For example, with a pressure inside the chamber set to 1 Torr (133.32 Pa) and a temperature of the substrate 10 set to 200 degrees C, the substrate 10 is exposed to SiH₂Cl₂ for 20 minutes. Upon exposure of the metal oxide resist film 20 of the substrate 10 to the silicon-containing gas, the metal constituting the metal oxide contained in the metal oxide resist film 20 is substituted with silicon. Further, a metal compound is generated as a by-product by the substitution. The metal compound as the by-product is vaporized and removed. For example, when the metal oxide resist film 20 is SnO_x, SnO₂ in the exposed portion 20a is substituted with SiO₂. In addition, SnCl₄ is generated as a by-product by the substitution. The SnCl₄ is vaporized and removed from the metal oxide resist film 20.

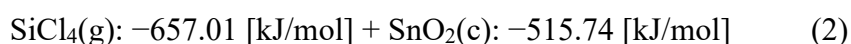
[0020] By substituting SnO₂ in the exposed portion 20a of the metal oxide resist film 20 with SiO₂ as described above, the exposed portion 20a can be processed by using conventional SiO₂ processing techniques. In addition, since residues such as SnO are also substituted with SiO₂, the residues can be removed by using conventional SiO₂ processing techniques. Accordingly, the substrate processing according to the embodiment can improve processability of the metal oxide resist film 20 used as a photoresist film in EUV exposure.

[0021] Here, a mechanism by which the substitution occurs is presumed. In the following description, a case will be described as an example in which SnO₂ in the exposed portion 20a of the metal oxide resist film 20 reacts with SiCl₄ formed from the silicon halide and the hydride included in the silicon-containing gas, as represented by reaction formula (1) below.



[0023] The Gibbs free energy before the reaction of reaction formula (1) can be expressed as shown in equation (2) below. In addition, the Gibbs free energy after the reaction of reaction formula (1) can be expressed as shown in equation (3) below.

[0024] Before reaction:



After reaction:



[0025] The total Gibbs free energy after the reaction is superior than that before the reaction. For this reason, it is presumed that the substitution represented by reaction formula (1) occurs.

[0026] Further, SnO₂ has a sufficiently higher vapor pressure than SiO₂. From this viewpoint as well, it is presumed that the substitution represented by reaction formula (1) occurs. In addition, since tin (Sn) and silicon (Si) both belong to group 14, it is presumed that the substitution readily occurs.

[0027] A rate at which SnO₂ in the exposed portion 20a of the metal oxide resist film 20 is substituted with SiO₂ varies according to the temperature of the substrate 10. FIGS. 4A and 4B are diagrams illustrating examples of a substitution state in the metal oxide resist film 20 of the substrate 10 according to the embodiment. FIG. 4A shows a high-angle annular dark field

scanning transmission electron microscopy (HAADF-STEM) image of the substrate 10 when the temperature of the substrate 10 is set to a low temperature of 150 degrees C or lower, together with an image showing a distribution of Sn and an image showing a distribution of Si. FIG. 4B shows a HAADF-STEM image of the substrate 10 when the temperature of the substrate 10 is set to a high temperature of 150 degrees C or higher, together with an image showing a distribution of Sn and an image showing a distribution of Si. As shown in FIG. 4B, at the high temperature, Sn is not distributed whereas Si is distributed, indicating that SnO₂ has been substituted with SiO₂ and that the substitution rate is high. In contrast, as shown in FIG. 4A, at the low temperature, both Sn and Si are distributed, indicating that the substitution rate is low.

[0028] For example, when the temperature of the substrate 10 is set to 50 degrees C, 100 degrees C, 150 degrees C, and 200 degrees C, respectively, and the substrate 10 is exposed to dichlorosilane gas at 5 Torr (666.61 Pa), the substitution rate at which SnO₂ in the exposed portion 20a of the metal oxide resist film 20 is substituted with SiO₂ are as follows:

[0029] 50 degrees C: 0.15 [nm/min]

100 degrees C: 0.45 [nm/min]

150 degrees C: 0.62 [nm/min]

200 degrees C: >0.62 [nm/min]

[0030] When the temperature of the substrate 10 is set to 200 degrees C, the exposed portion 20a is entirely substituted. Thus, the substitution rate at 200 degrees C is indicated as being greater than 0.62 [nm/min].

[0031] The substitution gradually progresses inward from a surface of the metal oxide resist film 20. As the temperature of the substrate 10 decreases, the substitution rate decreases, and a time required to substitute the entire exposed portion 20a increases. The temperature of the substrate 10 during the substitution may be 50 degrees C or higher. On the other hand, when the temperature of the substrate 10 is excessively high, the substrate 10 may suffer thermal damage. Therefore, an upper limit of the temperature of the substrate 10 may be set to a temperature at which the substrate does not suffer thermal damage. For example, the temperature of the substrate 10 during the substitution may be set within a range of 50 degrees C to 500 degrees C.

For a rapid substitution, the temperature of the substrate 10 may be set to 100 degrees C or higher, and specifically 200 degrees C or higher.

(Apparatus Configuration)

[0032] Next, an example of a configuration of a substrate processing apparatus 100 according to an embodiment will be described. FIG. 5 is a diagram illustrating an example of a schematic configuration of the substrate processing apparatus 100.

[0033] The substrate processing apparatus 100 includes a chamber 110, a gas supplier 120, a stage 130, and an exhauster 140. The substrate processing apparatus 100 further includes a gas introducer. The chamber 110 is configured to be airtight. The gas introducer is configured to introduce at least one processing gas into the chamber 110. The gas introducer includes a showerhead 113. The stage 130 is disposed inside the chamber 110. The showerhead 113 is disposed above the stage 130. In one embodiment, the showerhead 113 constitutes at least a portion of a ceiling of the chamber 110.

[0034] A placement surface 130a for supporting the substrate 10 is formed on an upper surface of the stage 130. The placement surface 130a is formed to be larger than the substrate 10. The chamber 110 is provided with a loading/unloading port (not shown), which can be opened and closed by a gate valve. When the substrate 10 is loaded into the substrate processing apparatus 100, the loading/unloading port (not shown) provided in the chamber 110 is set to be in an open state. The substrate 10 is loaded into the chamber 110 via the loading/unloading port by a transfer mechanism such as a transfer arm, and is placed on the placement surface 130a of the stage 130.

[0035] A heater 131 is provided inside the stage 130. A power supply 132 is connected to the heater 131. The power supply 132 supplies power to the heater 131. The heater 131 generates heat by the power supplied from the power supply 132. The power supply 132 is configured to control the power supplied to the heater 131. The substrate processing apparatus 100 is configured to control the temperature of the substrate 10 by controlling the power supplied from the power supply 132 to the heater 131 to control a temperature of the heater 131.

[0036] The showerhead 113 is configured to introduce at least one processing gas from the gas supplier 120 into the chamber 110. The showerhead 113 includes at least one gas supply port 113a, at least one gas diffusion chamber 113b, and a plurality of gas introduction ports 113c. The processing gas supplied to the gas supply port 113a passes through the gas diffusion chamber 113b and is introduced into the chamber 110 from the plurality of gas introduction ports 113c.

[0037] The gas supplier 120 includes at least one gas source 121 and at least one flow controller 122. The flow controller 122 may include, for example, a mass flow controller or a pressure-controlled flow controller. The gas supplier 120 supplies a silicon-containing gas from the gas source 121 to the showerhead 113 via the flow controller 122.

[0038] The exhauster 140 is connected to, for example, a gas discharge port 110a provided at a bottom of the chamber 110. The exhauster 140 may include a pressure regulating valve and a vacuum pump. The pressure inside the chamber 110 is adjusted by the pressure regulating valve. The vacuum pump may include a turbo molecular pump, a dry pump, or a combination thereof.

[0039] The substrate processing apparatus 100 includes a controller 150. The controller 150 controls individual components of the substrate processing apparatus 100 and causes the substrate processing apparatus 100 to perform the substrate processing.

(Substrate Processing)

[0040] Next, an example of substrate processing including a substrate processing method of the present disclosure will be described. FIG. 6 is a flowchart illustrating an example of substrate processing according to an embodiment. FIG. 6 illustrates a flow of substrate processing for forming a pattern on the substrate 10 as shown in FIG. 3.

[0041] A photoresist film containing a metal oxide is formed on the surface of the substrate 10 (step S10). For example, the substrate 10 is transferred to a film forming apparatus, and the metal oxide resist film 20, such as a tin oxide film, is formed on the substrate 10 in the film forming apparatus. The metal oxide resist film 20 may be formed on the substrate 10 by spin

coating, or may be formed on the substrate 10 by vacuum deposition.

[0042] Subsequently, EUV exposure is performed on the substrate 10 on which the photoresist film containing the metal oxide has been formed (step S11). For example, the substrate 10 is transferred to an EUV exposure apparatus, and EUV exposure is performed on the substrate 10 in the EUV exposure apparatus. In the EUV exposure, EUV light is irradiated onto the metal oxide resist film 20 of the substrate 10 via the mask 30 having a predetermined pattern.

[0043] Subsequently, post-exposure bake (PEB) is performed on the EUV-exposed substrate 10 (step S12). For example, the substrate 10 is transferred to a thermal processing apparatus, and post-exposure bake is performed on the substrate 10 in the thermal processing apparatus.

[0044] Subsequently, development of the substrate 10 on which the post-exposure bake has been performed is performed (step S13). For example, the substrate 10 is transferred to an etching apparatus, and the metal oxide resist film 20 of the substrate 10 is etched in the etching apparatus to develop the pattern formed on the metal oxide resist film 20.

[0045] Subsequently, the developed substrate 10 is exposed to a silicon-containing gas (step S14). For example, the substrate 10 is transferred to the substrate processing apparatus 100 and is placed on the stage 130. The substrate processing apparatus 100 reduces, by the exhauster 140, the pressure inside the chamber 110 to a predetermined pressure appropriate for exposure to the silicon-containing gas. Further, the substrate processing apparatus 100 controls the temperature of the heater 131 to control the temperature of the substrate 10 placed on the stage 130 to be within a range of 50 to 500 degrees C. Thereafter, the substrate processing apparatus 100 supplies the silicon-containing gas from the gas supplier 120 into the chamber 110 to expose the substrate 10 to the silicon-containing gas. For example, the substrate processing apparatus 100 sets the pressure inside the chamber 110 to be 1 Torr (133.32 Pa) and the temperature of the substrate 10 to be 200 degrees C, and exposes the substrate 10 to SiH_2Cl_2 gas for 20 minutes. As a result, the metal constituting the metal oxide contained in the developed metal oxide resist film 20 is substituted with silicon. For example, when the metal oxide resist film 20 is SnO_x , substitution with SiO_2 occurs.

[0046] Accordingly, the exposed portion 20a can be processed by using conventional SiO_2

processing techniques. As described above, the substrate processing according to the embodiment can improve processability of the metal oxide resist film 20 used as a photoresist film in EUV exposure.

[0047] Next, an example of processing of the substrate 10 on which a pattern has been formed will be described. In the following, as an example of processing of the substrate 10, a flow of substrate processing for performing double patterning on the substrate 10 will be described.

FIG. 7 is a diagram for explaining an example of a flow of substrate processing for performing double patterning on the substrate 10. In the metal oxide resist film 20 of the substrate 10, for example, a pattern has been formed by the exposed portion 20a through the substrate processing shown in FIG. 3. SnO_2 in the exposed portion 20a has been substituted with SiO_2 .

[0048] When performing double patterning on the substrate 10, for example, a SiN_x film 25 is formed on the substrate 10 by atomic layer deposition (ALD) or the like. On the substrate 10, the SiN_x film 25 is formed to cover unevenness caused by the exposed portion 20a of the metal oxide resist film 20. Subsequently, anisotropic etching of the SiN_x film 25 formed on the substrate 10 is performed by plasma etching or the like. By performing the anisotropic etching of the SiN_x film 25, on the substrate 10, the SiN_x film 25 on an upper surface of the exposed portion 20a of the metal oxide resist film 20 and the SiN_x film 25 on a recess between the exposed portions 20a are etched. By performing the anisotropic etching of the SiN_x film 25, the SiN_x film 25 on a sidewall of the exposed portion 20a remains on the substrate 10.

Subsequently, anisotropic etching of SiO_x is performed on the substrate 10 by plasma etching or the like. By performing the anisotropic etching of SiO_x , the exposed portion 20a is etched from an upper surface side thereof, and the SiN_x film 25, which had been the sidewall of the exposed portion 20a, remains on the substrate 10. In the double patterning of the substrate 10, the remaining SiN_x film 25 is used as a mask to pattern the substrate 10. Thus, fine processing on the substrate 10 can be achieved.

[0049] As described above, with the substrate processing method according to the embodiment, SnO_2 in the exposed portion 20a of the metal oxide resist film 20 is substituted with SiO_2 , and thus double patterning of the substrate 10 can be achieved.

[0050] In the above-described embodiment, a case has been mainly described by way of example in which the metal oxide resist film 20 is a tin oxide film. However, the disclosed technique is not limited thereto. It is presumed that the substitution described in the embodiment occurs in cases of elements having catenation properties. Catenation refers to that atoms of the same element are bonded to form a long chain. For example, the metal oxide resist film 20 may be an oxide film of any of W, Te, Sb, In, Zn, Zr, and Hf. In this case as well, with the substrate processing method according to the embodiment, oxides of W, Te, Sb, In, Zn, Zr, and Hf contained in the metal oxide resist film 20 may be substituted with silicon. Accordingly, processability of the photoresist film in EUV exposure can be improved.

[0051] In addition, in the above-described embodiment, a case has been described by way of example in which the substrate processing apparatus 100 is configured to expose substrates 10 one by one to the silicon-containing gas. However, the disclosed technique is not limited thereto. The substrate processing apparatus 100 may have a configuration in which a plurality of substrates 10 may be disposed inside the chamber 110, and may expose the plurality of substrates 10 to the silicon-containing gas.

[0052] Hereinabove, the embodiments have been described. As described above, the substrate processing method according to the embodiment includes a) (for example, step S14) and b) (for example, step S14). In a), the substrate 10 having a surface on which a photoresist film containing a metal oxide is formed is disposed in the chamber 110. In b), a silicon-containing gas is supplied into the chamber 110 to substitute a metal constituting the metal oxide contained in the photoresist film with silicon. Therefore, the substrate processing method according to the embodiment can improve processability of the photoresist film in EUV exposure.

[0053] Further, the photoresist film is the metal oxide resist film 20. The substrate processing method according to the embodiment further includes c) prior to a) and b). In c), EUV exposure is performed on the metal oxide resist film 20 formed on the surface of the substrate 10. Therefore, the substrate processing method according to the embodiment can improve processability of the metal oxide resist film 20 in EUV exposure.

[0054] The substrate processing method according to the embodiment further includes d) after c)

and before process b). In d), the EUV-exposed metal oxide resist film 20 is developed after c) and before process b). Therefore, the substrate processing method according to the embodiment can improve processability of the developed metal oxide resist film 20.

[0055] The metal oxide is an oxide of any of Sn, W, Te, Sb, In, Zn, Zr, and Hf. Accordingly, the substrate processing method according to the embodiment can substitute the metal constituting the metal oxide with silicon.

[0056] The metal oxide resist film 20 is a tin oxide film. Therefore, the substrate processing method according to the embodiment can substitute tin constituting the tin oxide film with silicon.

[0057] The gas includes a silicon halide and a hydride. In b), the metal oxide contained in the developed metal oxide resist film 20 is brought into contact with the silicon halide and the hydride, and a metal constituting the metal oxide is substituted with silicon. Therefore, the substrate processing method according to the embodiment can substitute the metal constituting the metal oxide with silicon.

[0058] The silicon halide and the hydride form a silicon oxide and are selected from SiCl_4 , SiH_2Cl_2 , SiF_4 , SiH_4 , Si_2H_6 , and Si_2Cl_6 . Therefore, the substrate processing method according to the embodiment can substitute the metal constituting the metal oxide with silicon.

[0059] In b), the substrate 10 is heated to 50 degrees C or higher, and the gas is supplied into the chamber 110 to substitute the metal constituting the metal oxide contained in the photoresist film with silicon. Therefore, the substrate processing method according to the embodiment can substitute the metal constituting the metal oxide with silicon.

[0060] The substrate processing method according to the embodiment further includes e) after b). In e), double patterning is performed on the photoresist film. Therefore, the substrate processing method according to the embodiment can form fine patterns in the photoresist film.

[0061] The substrate processing apparatus 100 according to the embodiment includes the chamber 110, the stage 130, and the gas supplier 120. The stage 130 is disposed inside the chamber 110, and the substrate 10 having a surface on which a photoresist film containing a metal oxide is formed is placed on the stage 130. The gas supplier 120 supplies a silicon-

containing gas into the chamber 110. Therefore, the substrate processing apparatus 100 according to the embodiment can improve processability of the photoresist film in EUV exposure.

(Others)

[0062] The technique disclosed herein is not limited to the above-described embodiments, and various modifications may be made within the scope of the gist thereof.

[0063] The embodiments disclosed herein are illustrative in all respects and should not be construed as limiting. Indeed, the above-described embodiments may be implemented in various forms. The above-described embodiments may be omitted, substituted, or modified in various ways without departing from the scope and spirit of the appended claims.

[0064] The following supplementary notes are provided with respect to the above-described embodiments.

(Supplementary Note 1)

[0065] A substrate processing method, including:

- a) placing a substrate, which has a surface on which a photoresist film containing a metal oxide is formed, in a chamber; and
- b) supplying a silicon-containing gas into the chamber to substitute a metal, which constitutes the metal oxide contained in the photoresist film, with silicon.

(Supplementary Note 2)

[0066] The substrate processing method of Supplementary Note 1, wherein the photoresist film is a metal oxide resist film, and

wherein the method further comprises, prior to a) and b), c) performing extreme ultra violet (EUV) exposure on the metal oxide resist film formed on the surface of the substrate.

(Supplementary Note 3)

[0067] The substrate processing method of Supplementary Note 2, further including, after c) and before b), d) developing the metal oxide resist film exposed to EUV.

(Supplementary Note 4)

[0068] The substrate processing method of any one of Supplementary Notes 1 to 3, wherein the metal oxide is an oxide of any of Sn, W, Te, Sb, In, Zn, Zr, and Hf.

(Supplementary Note 5)

[0069] The substrate processing method of Supplementary Note 2 or 3, wherein the metal oxide resist film is a tin oxide film.

(Supplementary Note 6)

[0070] The substrate processing method of Supplementary Note 3, wherein the gas includes a silicon halide and a hydride, and

wherein b) includes bringing the metal oxide contained in the developed metal oxide resist film into contact with the silicon halide and the hydride to substitute the metal constituting the metal oxide with silicon.

(Supplementary Note 7)

[0071] The substrate processing method of Supplementary Note 6, wherein the silicon halide and the hydride form a silicon oxide and are selected from the group consisting of SiCl_4 , SiH_2Cl_2 , SiF_4 , SiH_4 , Si_2H_6 , and Si_2Cl_6 .

(Supplementary Note 8)

[0072] The substrate processing method of any one of Supplementary Notes 1 to 7, wherein b) includes heating the substrate to 50 degrees C or higher and supplying the gas into the chamber to substitute the metal, which constitutes the metal oxide contained in the photoresist film, with silicon.

(Supplementary Note 9)

[0073] The substrate processing method of any one of Supplementary Note 1 to 8, further including, after b), e) performing double patterning of the photoresist film.

(Supplementary Note 10)

[0074] A substrate processing apparatus including:

a chamber;

a stage disposed in the chamber and configured to place a substrate, which has a surface on which a photoresist film containing a metal oxide is formed, on the stage; and

a gas supplier configured to supply a silicon-containing gas into the chamber.

EXPLANATION OF REFERENCE NUMERALS

[0075] 10: substrate, 11: silicon substrate, 12: first underlying film, 13: second underlying film, 20: metal oxide resist film, 20a: exposed portion, 20b: unexposed portion, 25: SiN_x film, 30: mask, 100: substrate processing apparatus, 110: chamber, 120: gas supplier, 130: stage, 130a: placement surface, 131: heater, 132: power supply, 140: exhauster, 150: controller

WHAT IS CLAIMED IS:

1. A substrate processing method, comprising:
 - a) placing a substrate, which has a surface on which a photoresist film containing a metal oxide is formed, in a chamber; and
 - b) supplying a silicon-containing gas into the chamber to substitute a metal, which constitutes the metal oxide contained in the photoresist film, with silicon.
2. The substrate processing method of Claim 1, wherein the photoresist film is a metal oxide resist film, and
 - wherein the substrate processing method further comprises, prior to a) and b), c) performing extreme ultra violet (EUV) exposure on the metal oxide resist film formed on the surface of the substrate.
3. The substrate processing method of Claim 2, further comprising, after c) and before b),
 - d) developing the metal oxide resist film exposed to EUV.
4. The substrate processing method of Claim 1, wherein the metal oxide is an oxide of any of Sn, W, Te, Sb, In, Zn, Zr, and Hf.
5. The substrate processing method of Claim 2, wherein the metal oxide resist film is a tin oxide film.
6. The substrate processing method of Claim 3, wherein the gas includes a silicon halide and a hydride, and
 - wherein b) includes bringing the metal oxide contained in the developed metal oxide resist film into contact with the silicon halide and the hydride to substitute the metal constituting the metal oxide with silicon.

7. The substrate processing method of Claim 6, wherein the silicon halide and the hydride form a silicon oxide and are selected from the group consisting of SiCl_4 , SiH_2Cl_2 , SiF_4 , SiH_4 , Si_2H_6 , and Si_2Cl_6 .
8. The substrate processing method of Claim 1, wherein b) includes heating the substrate to 50 degrees C or higher and supplying the gas into the chamber to substitute the metal constituting the metal oxide contained in the photoresist film with silicon.
9. The substrate processing method of Claim 1, further comprising, after b), e) performing double patterning of the photoresist film.
10. A substrate processing apparatus comprising:
a chamber;
a stage disposed in the chamber and configured to place a substrate, which has a surface on which a photoresist film containing a metal oxide is formed, on the stage; and
a gas supplier configured to supply a silicon-containing gas into the chamber.