

SUBSTRATE AND SUBSTRATE PROCESSING METHOD

TECHNICAL FIELD

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

BACKGROUND

[0002] Patent Document 1 discloses "a method of manufacturing a patterning structure, including providing a substrate to receive a pattern, incorporating a radiation-absorbing layer in a surface of the substrate, and providing an imaging layer, wherein the radiation-absorbing layer is provided below the imaging layer to increase radiation absorptivity and/or patterning performance of the imaging layer."

[Prior Art Documents]

[Patent Document]

[0003] Patent Document 1: Japanese Patent Laid-Open Publication No. 2022-550568

[Non-Patent Document]

[0004] Non-Patent Document 1: B. L. Henke, E. M. Gullikson, and J. C. Davis, "X-Ray Interactions: Photoabsorption, Scattering, Transmission and Reflection $E = 50\text{-}30,000$ eV, $Z = 1\text{-}92$," Atomic Data and Nuclear Data Tables Volume 54 Issue 2 Pages 181-342, July 1993.

SUMMARY

[0005] The present disclosure provides a substrate and a substrate processing method capable of oxidizing a photoresist film during exposure.

[0006] A substrate according to one embodiment of the present disclosure includes a photoresist film and an organic film. The photoresist film includes a first metal oxide and reacts with extreme ultraviolet (EUV) light. The organic film is provided under the photoresist film, and includes a second metal oxide which has metal-oxygen binding energy lower than metal-oxygen

binding energy of the first metal oxide constituting the photoresist film, and from which oxygen is dissociated by the EUV light.

[0007] According to the present disclosure, it is possible to oxidize a photoresist film during exposure.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIG. 1 is a diagram illustrating an atomic absorption cross section of EUV light.

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

FIG. 3 is a diagram for explaining a case in which a substrate according to the embodiment is subjected to EUV exposure.

FIG. 4 is a diagram for explaining an example of a case in which a metal oxide of an organic film of a substrate according to the embodiment is unevenly distributed.

FIG. 5 is a diagram illustrating an example of a verification result according to the embodiment.

FIG. 6 is a view illustrating an example of a schematic configuration of a film forming apparatus according to an embodiment.

FIG. 7 is a diagram illustrating an example of a substrate processing flow according to an embodiment.

FIGS. 8A to 8F are diagrams illustrating an example of change in a substrate by substrate processing according to the embodiment.

DETAILED DESCRIPTION

[0009] Hereinafter, embodiments of a substrate and a substrate processing method disclosed herein will be described in detail with reference to the drawings. However, the substrate and substrate processing method disclosed herein are not limited by the embodiments.

[0010] In manufacturing a semiconductor device, a pattern is 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, a pattern having a predetermined shape is formed on the photoresist film by subjecting the formed photoresist film to selective exposure via a mask having a predetermined pattern and a development process. In the related art, a carbon-based photoresist has been used for the photoresist film. For example, in the related art, a chemically amplified resist has been used for the photoresist film.

[0011] In recent years, with miniaturization of semiconductor devices, miniaturization has also progressed using lithography technology. As a miniaturization technique, shortening a wavelength of an exposure light source may be used. Recently, extreme ultraviolet (EUV) exposure using EUV light has been performed.

[0012] However, since a carbon-based photoresist film in the related art has poor absorption of EUV, a reaction takes a long time. Therefore, in the EUV exposure, a photoresist film containing a metal oxide is used. For example, in the EUV exposure, a metal oxide resist (MOR) such as a tin oxide is used for the photoresist film.

[0013] Here, Non-Patent Document 1 discloses an atomic absorption cross section of EUV light. FIG. 1 is a diagram illustrating an atomic absorption cross section of EUV light. A horizontal axis of FIG. 1 represents an atomic number of each atom. The horizontal axis of FIG. 1 represents an atomic absorption cross section. The absorption cross section indicates a ratio at which EUV light is absorbed upon passing through an atom. In FIG. 1, the atomic absorption cross sections for respective atomic numbers are shown with respect to each atomic number. For example, the absorption cross section for atomic number 12 is the absorption cross section of carbon. The absorption cross section for atomic number 50 is the absorption cross section of tin. Tin has a larger absorption cross section of EUV light than carbon. That is, tin has a higher EUV absorption rate than carbon.

[0014] In EUV exposure, a substrate on which a photoresist film has been formed is transferred to an EUV exposure apparatus, and the photoresist film is irradiated with EUV light in the EUV

exposure apparatus to perform the exposure. Thereafter, the substrate is taken out from the EUV exposure apparatus and subjected to post exposure bake (PEB). In the PEB, the substrate after the EUV exposure is heated to promote a reaction with oxygen in an exposed portion of the photoresist film.

[0015] Here, in view of a development mechanism, it is desirable to oxidize the photoresist film immediately after the exposure. However, since the EUV exposure apparatus performs the EUV exposure of the substrate in a state in which an interior of the EUV exposure apparatus is maintained at a high degree of vacuum, it is difficult to cause a gas that promotes oxidation to flow, and oxidation of the photoresist film does not proceed during the exposure. Since oxygen is generally supplied to the photoresist film by the PEB or the like after the exposure, when the photoresist film can be oxidized during the exposure, oxidation of the photoresist film can be performed in-situ in a chamber of the EUV exposure apparatus. Further, when a metal oxide and the photoresist film are combined, an anchor is formed, and thus adhesion is improved.

[0016] Therefore, a technique for oxidizing a photoresist film during exposure is provided.

(Embodiments)

[0017] Embodiments will 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 illustrating an example of the substrate 10 according to an embodiment. In the substrate 10, a first underlayer film 12, a second underlayer film 13, and an organic film 14 are sequentially stacked over a silicon substrate 11. The first underlayer film 12 is, for example, a spin-on carbon (SOC) film or a low-density amorphous carbon (a-C) film. The second underlayer film 13 is, for example, an organic film, a SiC film, a SiON film, or a SiOCN film. The organic film 14 is, for example, a diamond-like carbon (DLC) film or an a-C film. The organic film 14 serves as an underlying layer of a photoresist film described later. The first underlayer film 12, the second underlayer film 13, and the organic film 14 are not limited to the above-described examples. The configuration of the substrate 10 shown in FIG. 2 is merely an example, and the present

disclosure is not limited thereto. Films necessary for manufacturing a semiconductor device are formed on the substrate 10 as required.

[0018] When 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 one of tin (Sn), tungsten (W), tellurium (Te), antimony (Sb), indium (In), zinc (Zn), zirconium (Zr), indium (In), and hafnium (Hf). For example, in EUV exposure, a metal oxide resist film 20 is formed as the photoresist film on the surface of the substrate 10. For example, a tin oxide film is formed as the metal oxide resist film 20 on the substrate 10.

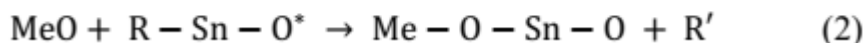
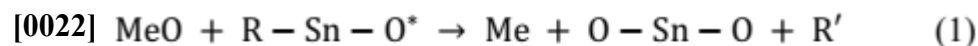
[0019] In the EUV exposure, the substrate 10 on which the metal oxide resist film 20 has been formed is transferred to an EUV exposure apparatus, and the EUV exposure apparatus performs exposure by irradiating the metal oxide resist film 20 with EUV light. Since the EUV exposure apparatus performs the EUV exposure in a state in which an interior of the EUV exposure apparatus is maintained at a high degree of vacuum, it is difficult to cause a gas that promotes oxidation to flow, and a reaction with oxygen in an exposed portion of the metal oxide resist film 20 does not proceed.

[0020] Therefore, in the substrate 10 according to the embodiment, the organic film 14 contains a metal oxide which has metal-oxygen binding energy lower than that of a metal oxide contained in the metal oxide resist film 20, and from which oxygen is dissociated by EUV light. For example, when the metal oxide resist film 20 is a tin oxide (SnO_x) film, the organic film 14 contains a metal oxide which has metal-oxygen binding energy lower than that of the tin oxide, and from which oxygen is dissociated by EUV light. Examples of the metal oxide contained in the organic film 14 include an oxide of cesium (Cs), i.e., CsO_x , an oxide of tellurium (Te), i.e., TeO_x , and an oxide of selenium (Se), i.e., SeO_x .

[0021] FIG. 3 is a diagram illustrating a case in which the substrate 10 according to the embodiment is subjected to EUV exposure. FIG. 3 illustrates the organic film 14 and the metal oxide resist film 20, which are portions of the substrate 10 according to the embodiment. The

metal oxide resist film 20 contains a compound (Sn-R) of Sn and a ligand R such as CH_X. When the substrate 10 according to the embodiment is subjected to the EUV exposure, in an exposed portion of the metal oxide resist film 20, Sn and the ligand R are cleaved. Further, secondary electrons are generated from a metal oxide MeO such as CsO_X, TeO_X, or SeO_X contained in the organic film 14, and some of the secondary electrons are supplied to the metal oxide resist film 20 to assist a reaction of the metal oxide resist film 20. Further, when the substrate 10 according to the embodiment is subjected to the EUV exposure, oxygen is dissociated from the metal oxide of the organic film 14, and an oxygen reaction proceeds in the exposed portion of the metal oxide resist film 20. For example, in the exposed portion of the metal oxide resist film 20, oxygen is supplied from the metal oxide MeO contained in the organic film 14, and causes a reaction represented by Chemical Formula (1). In addition, at an interface between the metal oxide resist film 20 and the organic film 14, a reaction such as Chemical Formula (2) occurs together with Chemical Formula (1), and the metal oxide and the resist are combined to form an anchor, and thus adhesion is improved.

[Chemical Formula 1]



[0023] In the substrate 10 according to the embodiment, it is possible to oxidize the metal oxide resist film 20 during the exposure by using the organic film 14 that contains the metal oxide as described above.

[0024] In the organic film 14, as a content of the metal oxide increases, an amount of secondary electrons or oxygen generated by the EUV exposure increases. However, when the content of the metal oxide in the organic film 14 is high, properties of the metal oxide appear and properties as an organic film deteriorate. Therefore, the content of the metal oxide in the organic film 14 may be 1 to 20 atomic %, and specifically 5 to 10 atomic %.

[0025] Further, when the EUV exposure is performed, secondary electrons and oxygen generated in a portion of the organic film 14 close to the metal oxide resist film 20 reach the metal oxide resist film 20. Therefore, the metal oxide of the organic film 14 may be unevenly

distributed on a side of the metal oxide resist film 20. For example, the metal oxide may be unevenly distributed within a range of 20 nm from the interface between the organic film 14 and the metal oxide resist film 20, specifically, within a range of 5 nm.

[0026] FIG. 4 is a diagram illustrating an example of a case in which a metal oxide of the organic film 14 of the substrate 10 according to the embodiment is unevenly distributed. FIG. 4 schematically shows a metal oxide 14a contained in the organic film 14. In addition, FIG. 4 shows a concentration distribution of the metal oxide 14a with respect to a depth from the interface with the metal oxide resist film 20. In FIG. 4, a case is shown in which the metal oxide 14a is contained within a range of 5 nm from the interface between the metal oxide resist film 20 and the organic film 14, such that a concentration of the metal oxide 14a gradually increases toward the interface and reaches a maximum of 10 atomic %.

[0027] By unevenly distributing the metal oxide of the organic film 14 on the side of the metal oxide resist film 20 as described above, the metal oxide resist film 20 can be oxidized during the exposure while maintaining functions of the organic film 14.

[0028] Oxides of Cs, Te, and Se differ in ease of oxygen dissociation according to oxidization numbers. Therefore, with respect to the oxides of Sn, Cs, Te, and Se, Gibbs free energy was calculated to verify whether an oxidation reaction would occur. FIG. 5 is a diagram illustrating an example of the verification result according to the embodiment. FIG. 5 illustrates Gibbs free energy in cases of reacting Sn into SnO_2 and reacting SnO into SnO_2 with respect to Cs_2O , Cs_2O_2 , Cs_2O_3 , CsO_2 , CsO_3 , TeO , TeO_2 , TeO_3 , SeO_2 , and SeO_3 . When the Gibbs free energy has a negative value, a reaction that oxidizes Sn occurs. For example, Cs_2O_2 , Cs_2O_3 , CsO_2 , CsO_3 , TeO , TeO_2 , TeO_3 , SeO_2 , and SeO_3 can react Sn into SnO_2 and can also react SnO into SnO_2 . That is, when the metal oxide resist film 20 is a tin oxide film, the metal oxide contained in the organic film 14 may be any one of an oxide of Cs having a valence of 2 or more, an oxide of Te, and an oxide of Se.

[0029] The metal oxide contained in the organic film 14 may be stable in the organic film 14. Here, stability of the oxide of Cs will now be described. Cs_2O , Cs_2O_2 , Cs_2O_3 , and CsO_2 are

stable at room temperature. On the other hand, CsO_3 is gradually decomposed into CsO_2 at room temperature. Therefore, when the oxide of Cs is used as the metal oxide contained in the organic film 14, any one of Cs_2O_2 , Cs_2O_3 , and CsO_2 may be used.

(Apparatus Configuration)

[0030] Next, an example of a configuration of a film forming apparatus 100 for forming the organic film 14 according to an embodiment will be described. FIG. 6 is a view illustrating a schematic exemplary configuration of the film forming apparatus 100 according to the embodiment.

[0031] The film forming apparatus 100 includes a grounded cylindrical vacuum container 101 made of, for example, aluminum. At a bottom of the vacuum container 101, a susceptor 102 for placing the substrate 10 thereon is provided. The susceptor 102 is made of, for example, aluminum and is formed in a substantially cylindrical shape. The susceptor 102 also functions as a lower electrode of a parallel-plate electrode. An electrostatic chuck 103 is provided in an upper surface of the susceptor 102. The electrostatic chuck 103 is configured by embedding an electrode 131 in a thin dielectric layer. The electrode 131 is connected to a direct current (DC) voltage source 133 via a switch 132. As the switch 132 is turned on and a DC voltage is applied from the DC voltage source 133 to the electrode 131, the electrostatic chuck 103 electrostatically attracts the substrate 10. Holes 134 for a heat transfer gas are formed in the electrostatic chuck 103 at a plurality of locations. The heat transfer gas (e.g., helium gas) from a heat transfer gas supply pipe 135 is supplied to the holes 134. The electrostatic chuck 103 is configured to supply the heat transfer gas supplied from the heat transfer gas supply pipe 135 to a minute gap between the substrate 10 and the electrostatic chuck 103 via the holes 134. Although not shown, a lift pin for delivering the substrate 10 are provided to move up and down through the electrostatic chuck 103 and the susceptor 102.

[0032] The susceptor 102 has a flow path 121 formed therein. A coolant supply pipe 122 is connected to one end of the flow path 121 of the susceptor 102, and a coolant discharge pipe 123 is connected to the other end of the flow path 121. A coolant supplied from the coolant supply

pipe 122 is discharged from the coolant discharge pipe 123 via the flow path 121 of the susceptor 102. A temperature of the substrate 10 is adjusted by, for example, cooling by the coolant and heat transfer efficiency of the heat transfer gas between the substrate 10 and the electrostatic chuck 103. A ring 124 made of an insulating material is provided at an upper peripheral portion of the susceptor 102 to effectively implant reactive ions into the substrate 10.

[0033] The susceptor 102 is inserted into a flat cylindrical insulator 125 having an open upper surface to be insulated from the vacuum container 101. A matcher 141 and a first radio-frequency power supply 104 are connected between the susceptor 102 as the lower electrode and a reference potential, for example, the ground. The first radio-frequency power supply 104 is configured to generate radio-frequency power LF for biasing. A frequency of the radio-frequency power LF may be same as or different from a frequency of radio-frequency power HF for plasma generation described later. In one embodiment, the radio-frequency power LF has a frequency lower than that of the radio-frequency power HF. In one embodiment, the radio-frequency power HF has a frequency within a range of 100 kHz to 60 MHz.

[0034] An electrode plate 151 in parallel with the susceptor 102 is provided at a ceiling of the vacuum container 101 to face the susceptor 102. The electrode plate 151 constitutes an upper electrode of the parallel-plate electrode. The electrode plate 151 is made of aluminum coated with a dielectric (e.g., SiO₂). The electrode plate 151 is provided with a plurality of gas supply holes 152. The electrode plate 151 is supported by an electrode support 153 made of a conductor. A space is formed between the electrode plate 151 and the electrode support 153, and a gas diffusion plate 154 is disposed to divide the space vertically into two spaces. The gas diffusion plate 154 is provided with a plurality of gas holes 156. A gas supply pipe 106 is connected to the electrode support 153. The gas supply pipe 106 is connected to the electrode support 153 to supply a process gas into a space between the electrode support 153 and the gas diffusion plate 154. The process gas supplied from the gas supply pipe 106 is diffused and supplied into a space between the electrode plate 151 and the gas diffusion plate 154 via the plurality of gas holes 156 of the gas diffusion plate 154. The process gas supplied into the space

between the electrode plate 151 and the gas diffusion plate 154 is then supplied into a processing space via the gas supply holes 152 of the electrode plate 151. The electrode plate 151 and the electrode support 153 are insulated from the vacuum container 101 by an insulator 155.

[0035] A matcher 171 and a second radio-frequency power supply 107 are connected between the electrode plate 151 as the upper electrode and the reference potential, for example, the ground. The second radio-frequency power supply 107 is configured to generate the radio-frequency power HF for plasma generation. In one embodiment, the radio-frequency power HF has a frequency within a range of 10 MHz to 150 MHz.

[0036] A valve V is provided in the gas supply pipe 106. The gas supply pipe 106 is connected to a gas supply 160. The gas supply 160 is provided with one or more gas sources capable of supplying various process gases for use in film formation. Each gas source is connected to the gas supply pipe 106 via a flow rate controller. The flow rate controller may include, for example, a mass flow controller or a pressure-controlled flow rate controller. The gas supply 160 supplies various gases from the respective gas sources to the gas supply pipe 106 via the flow rate controllers.

[0037] An exhaust pipe 111 is connected to a bottom of the vacuum container 101. The exhaust pipe 111 is connected to a vacuum pump 112. An interior of the vacuum container 101 is evacuated by the vacuum pump 112 via the exhaust pipe 111.

[0038] Next, a flow of forming the organic film 14 on the substrate 10 in the film forming apparatus 100 will be briefly described. Films up to the second underlayer film 13 have been formed on the substrate 10. The substrate 10 is loaded into the vacuum container 101, which is maintained to a predetermined degree of vacuum in advance, from a load lock chamber (not shown) adjacent to the vacuum container 101. Further, the substrate 10 is placed on the susceptor 102 by raising and lowering operations of the lift pin (not shown). The susceptor 102 is adjusted in advance to a predetermined temperature. By turning the switch 132 on and applying a DC voltage to the electrode 131, the substrate 10 is attracted and held by the electrostatic chuck 103.

[0039] The film forming apparatus 100 opens the valve V, and while supplying various gases for use in forming the organic film 14 from the gas supply pipe 106, supplies the radio-frequency power HF and the radio-frequency power LF from the first radio-frequency power supply 104 and the second radio-frequency power supply 107 to form the organic film 14.

[0040] Below, an example of conditions for a process of forming the organic film 14 is shown.

- Processing condition

Temperature of the susceptor 102: 60 degrees C

Pressure in the vacuum container 101: 3 Pa

Power of the radio-frequency power HF: 400 W

Power of the radio-frequency power LF: less than 60 W

[0041] ▪ First gas condition

Ar gas containing C₂H₂ (10%): 500 sccm (8.34x10⁻⁶ m³/s)

Ar gas: 80 sccm

Processing time: 50 seconds

[0042] ▪ Second gas condition

Ar gas containing C₂H₂ (10%): 500 sccm

Ar gas: 80 sccm

Te(CH₃)₂ gas: 0 to 5 sccm (increased by 1 sccm every second)

Processing time: 5 seconds

[0043] The film forming apparatus 100 starts forming the organic film 14 under the processing condition described above, forms a lower portion of the organic film 14 by supplying various gases under the first gas condition, and forms an upper portion of the organic film 14 by supplying various gases under the second gas condition, thereby forming the organic film 14 with the metal oxide unevenly distributed therein. Accordingly, it is possible to form the organic film 14, in which the metal oxide is unevenly distributed, for example, as shown in FIG. 4, on the substrate 10.

[0044] The substrate 10 on which the organic film 14 has been formed is unloaded from the film forming apparatus 100 in a reverse order of the loading procedure. After the substrate 10 is

unloaded, the film forming apparatus 100 supplies oxygen gas from the gas supply pipe 106 to perform cleaning inside the vacuum container 101.

(Substrate Processing)

[0045] Next, an example of substrate processing including a substrate processing method of the present disclosure will be described. FIG. 7 is a diagram illustrating an example of a substrate processing flow according to an embodiment. FIGS. 8A to 8F are diagrams illustrating an example of change in the substrate 10 by the substrate processing according to the embodiment. As shown in FIG. 8A, films up to the second underlayer film 13 have been formed on the substrate 10.

[0046] The organic film 14 containing a metal oxide is formed on the substrate 10 (step S10). For example, the substrate 10 is transferred to the film forming apparatus 100, and by the film forming apparatus 100, the organic film 14 containing the metal oxide, which is any one of an oxide of Cs having a valence of 2 or more, an oxide of Te, and an oxide of Se, is formed on the second underlayer film 13 of the substrate 10. For example, as described above, the organic film 14 is formed such that the metal oxide is unevenly distributed on a side of an upper surface of the organic film 14. As a result, as shown in FIG. 8B, the organic film 14 is formed on the second underlayer film 13 of the substrate 10.

[0047] Subsequently, a photoresist film containing a metal oxide is formed on the substrate 10 (step S11). For example, the substrate 10 is transferred to a film forming apparatus, and in the film forming apparatus, the metal oxide resist film 20, such as a tin oxide film, is formed on the substrate 10. 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 film formation. As a result, as shown in FIG. 8C, the metal oxide resist film 20 is formed on the organic film 14 of the substrate 10.

[0048] Subsequently, the substrate 10 is subjected to EUV exposure (step S12). For example, the substrate 10 is transferred to an EUV exposure apparatus, and the substrate 10 is subjected to the EUV exposure in the EUV exposure apparatus. In the EUV exposure, as shown in FIG. 8D, the metal oxide resist film 20 of the substrate 10 is irradiated with EUV light via a mask 30

having a predetermined pattern. In the metal oxide resist film 20, an exposed portion 21a exposed to EUV light and an unexposed portion 21b not exposed to EUV light are formed in correspondence to the mask 30, as shown FIG. 8E. When the organic film 14 is subjected to the EUV exposure, secondary electrons are generated from the metal oxide of the exposed portion 21a, and oxygen is dissociated from the metal oxide of the exposed portion 21a. Therefore, in the metal oxide resist film 20, an oxygen reaction proceeds in the exposed portion. Accordingly, it is possible to oxidize the metal oxide resist film 20 in the substrate 10 during the exposure.

[0049] After the EUV exposure, PEB is performed on the substrate 10 (step S13). The PEB, which is generally performed in a photolithography process, is known to have an effect of promoting a chemical reaction caused by the exposure. In the present embodiment, due to characteristics of chemical species used, the PEB may be performed at a set temperature within a range of 100 to 300 degrees C, which is higher than in a usual case. By performing heating in a stepwise manner, for example, at 180 degrees C for 60 seconds followed by 250 degrees C for 60 seconds, a rate of a chemical reaction can be more effectively controlled even in a relatively high temperature range, and thus, it is possible to form a desired size of pattern with higher precision.

[0050] Subsequently, the photoresist film is developed (step S14). For example, the metal oxide resist film 20 has a difference in etch rate between the exposed portion 21a and the unexposed portion 21b. By etching the metal oxide resist film 20 by using the selectivity between the exposed portion 21a and the unexposed portion 21b, the metal oxide resist film 20 is developed. 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. As a result, the pattern formed in the metal oxide resist film 20 is developed. FIG. 8F shows a case in which negative-tone development is performed to leave the exposed portion 21a of the metal oxide resist film 20.

[0051] Thereafter, patterning is performed on the substrate 10 by using the pattern of the metal oxide resist film 20 developed as described above. For example, the first underlayer film 12,

the second underlayer film 13, and the organic film 14 are etched by using the pattern of the metal oxide resist film 20.

[0052] In the above embodiment, the case in which the metal oxide resist film 20 is a tin oxide film has mainly been described as an example. However, the technology of the present disclosure is not limited thereto. The metal oxide resist film 20 may be an oxide of any one of Sn, W, Te, Sb, In, Zn, Zr, In, and Hf. In this case, a metal oxide contained in the organic film 14 may be any metal oxide which has metal-oxygen binding energy lower than that of a metal oxide of the metal oxide resist film 20, and from which oxygen is dissociated by EUV light.

[0053] In addition, in the above embodiment, the case in which a photoresist film is the metal oxide resist film 20 has mainly been described as an example. However, the technology of the present disclosure is not limited thereto. The photoresist film may be any film that contains a metal oxide and reacts with EUV light. For example, the photoresist film may be a chemically amplified resist containing a metal oxide. The metal oxide contained in the photoresist film may be a metal oxide having a high absorption rate for EUV and may be, for example, an oxide of any one of Sn, Sn, W, Te, Sb, In, Zn, Zr, In, and Hf.

[0054] Hereinabove, the embodiments have been described. As described above, the substrate 10 according to the embodiment includes a photoresist film and the organic film 14. The photoresist film includes a first metal oxide and reacts with EUV light. The organic film 14 is formed under the photoresist film and includes a second metal oxide which has metal-oxygen binding energy lower than that of the first metal oxide constituting the photoresist film, and from which oxygen is dissociated by EUV light. Therefore, in the substrate 10 according to the embodiment, it is possible to oxidize the photoresist film during the exposure.

[0055] In addition, the photoresist film is the metal oxide resist film 20. Therefore, in the substrate 10 according to the embodiment, it is possible to oxidize the metal oxide resist film 20 during the exposure.

[0056] In addition, the organic film 14 constitutes an underlying layer of the metal oxide resist film 20. Therefore, in the substrate 10 according to the embodiment, it is possible to oxidize the metal oxide resist film 20 during the exposure.

[0057] In addition, the second metal oxide of the organic film 14 is unevenly distributed on the side of the metal oxide resist film 20. Further, the second metal oxide of the organic film 14 is unevenly distributed within the range of 5 nm from the interface between the organic film 14 and the metal oxide resist film 20. Further, the concentration of the second metal oxide of the organic film 14 increases toward the interface between the organic film 14 and the metal oxide resist film 20. Therefore, in the substrate 10 according to the embodiment, it is possible to oxidize the metal oxide resist film 20 during the exposure while maintaining functions of the organic film 14.

[0058] In addition, the first metal oxide is an oxide of Sn. Further, the second metal oxide is any one of an oxide of Cs having a valence of 2 or more, an oxide of Te, and an oxide of Se. Further, the oxide of Cs having the valence of 2 or more is any one of Cs_2O_2 , Cs_2O_3 , and CsO_2 . Therefore, in the substrate 10 according to the embodiment, it is possible to oxidize the oxide of Sn contained in the photoresist film during the exposure.

(Others)

[0059] The technology disclosed herein is not limited to the above-described embodiments, and numerous modifications can be made within the scope of the gist thereof.

[0060] It should be noted that the embodiments disclosed herein is exemplary in all aspects and is not restrictive. In practice, the above-described embodiments can be implemented in various forms. The above-described embodiments may be omitted, replaced, or modified in various forms without departing from the scope and spirit of the appended claims.

[0061] Regarding the above-described embodiments, the following supplementary notes are also disclosed.

(Supplementary note 1)

[0062] A substrate including:

 a photoresist film including a first metal oxide and reacting with extreme ultraviolet (EUV) light; and

 an organic film provided under the photoresist film, and including a second metal oxide which has metal-oxygen binding energy lower than metal-oxygen binding energy of the first metal oxide constituting the photoresist film, and from which oxygen is dissociated by the EUV light.

(Supplementary note 2)

[0063] The substrate of Supplementary note 1, wherein the photoresist film is a metal oxide resist film.

(Supplementary note 3)

[0064] The substrate of Supplementary note 2, wherein the organic film constitutes an underlying layer of the metal oxide resist film.

(Supplementary note 4)

[0065] The substrate of Supplementary note 3, wherein the second metal oxide of the organic film is unevenly distributed on a side of the metal oxide resist film.

(Supplementary note 5)

[0066] The substrate of Supplementary note 4, wherein the second metal oxide of the organic film is unevenly distributed within a range of 5 nm from an interface between the organic film and the metal oxide resist film.

(Supplementary note 6)

[0067] The substrate of Supplementary note 4 or 5, wherein a concentration of the second metal oxide of the organic film increases toward an interface between the organic film and the metal oxide resist film.

(Supplementary note 7)

[0068] The substrate of any one of Supplementary notes 1 to 6, wherein the first metal oxide is an oxide of Sn.

(Supplementary note 8)

[0069] The substrate of Supplementary note 7, wherein the second metal oxide is any one of an oxide of Cs having a valence of 2 or more, an oxide of Te, and an oxide of Se.

(Supplementary note 9)

[0070] The substrate of Supplementary note 8, wherein the oxide of Cs having the valence of 2 or more is any one of Cs_2O_2 , Cs_2O_3 , and CsO_2 .

(Supplementary note 10)

[0071] A substrate processing method of forming a pattern in a photoresist film that includes a first metal oxide and reacts with extreme ultraviolet (EUV) light, the method including:

- a) forming, on a substrate, an organic film including a second metal oxide which has metal-oxygen binding energy lower than metal-oxygen binding energy of the first metal oxide, and from which oxygen is dissociated by EUV light;
- b) forming the photoresist film on the organic film of the substrate;
- c) irradiating the photoresist film with the EUV light via a mask having a predetermined pattern;
- d) heating the photoresist film irradiated with the EUV light; and
- e) developing the heated photoresist film to form the pattern.

EXPLANATION OF REFERENCE NUMERALS

[0072] 10: substrate, 11: silicon substrate, 12: first underlayer film, 13: second underlayer film, 14: organic film, 14a: metal oxide, 20: metal oxide resist film, 30: mask, 100: film forming apparatus

WHAT IS CLAIMED IS:

1. A substrate comprising:
a photoresist film including a first metal oxide and reacting with extreme ultraviolet (EUV) light; and
an organic film provided under the photoresist film, and including a second metal oxide which has metal-oxygen binding energy lower than metal-oxygen binding energy of the first metal oxide constituting the photoresist film, and from which oxygen is dissociated by the EUV light.
2. The substrate of Claim 1, wherein the photoresist film is a metal oxide resist film.
3. The substrate of Claim 2, wherein the organic film constitutes an underlying layer of the metal oxide resist film.
4. The substrate of Claim 3, wherein the second metal oxide of the organic film is unevenly distributed on a side of the metal oxide resist film.
5. The substrate of Claim 4, wherein the second metal oxide of the organic film is unevenly distributed within a range of 5 nm from an interface between the organic film and the metal oxide resist film.
6. The substrate of Claim 4, wherein a concentration of the second metal oxide of the organic film increases toward an interface between the organic film and the metal oxide resist film.
7. The substrate of Claim 1, wherein the first metal oxide is an oxide of Sn.

8. The substrate of Claim 7, wherein the second metal oxide is any one of an oxide of Cs having a valence of 2 or more, an oxide of Te, and an oxide of Se.
9. The substrate of Claim 8, wherein the oxide of Cs having the valence of 2 or more is any one of Cs_2O_2 , Cs_2O_3 , and CsO_2 .
10. A substrate processing method of forming a pattern in a photoresist film that includes a first metal oxide and reacts with extreme ultraviolet (EUV) light, the method comprising:
- a) forming, on a substrate, an organic film including a second metal oxide which has metal-oxygen binding energy lower than metal-oxygen binding energy of the first metal oxide constituting the photoresist film, and from which oxygen is dissociated by EUV light;
 - b) forming the photoresist film on the organic film of the substrate;
 - c) irradiating the photoresist film with the EUV light via a mask having a predetermined pattern;
 - d) heating the photoresist film irradiated with the EUV light; and
 - e) developing the heated photoresist film to form the pattern.