

METHOD FOR STARTING UP FILM FORMING APPARATUS, METHOD FOR  
MANUFACTURING MASK BLANK, METHOD FOR MANUFACTURING  
TRANSFER MASK, AND METHOD FOR MANUFACTURING  
SEMICONDUCTOR DEVICE

Technical Field

[0001]

The present invention mainly relates to a method for starting up a film forming apparatus used to manufacture a mask blank. The present invention also relates to a method for manufacturing a mask blank using the film forming apparatus started up by the above starting-up method. The present invention further relates to a method for manufacturing a phase shift mask using the mask blank, and a method for manufacturing a semiconductor device using the phase shift mask.

Background Art

[0002]

In a manufacturing process of a semiconductor device, a fine pattern is generally formed using a photolithographic method. In the formation of the fine pattern, multiple transfer masks are usually used. Refinement of a pattern for the semiconductor device requires the refinement of a mask pattern formed in the transfer mask as well as shortening of a wavelength of an exposure light source used in photolithography. Nowadays, the exposure light sources used in the manufacture of semiconductor devices are shifting from KrF excimer lasers (wavelength: 248nm) to ArF excimer lasers (wavelength: 193nm), that is, shorter wavelength light sources are increasingly used.

[0003]

A mask blank serving as a master copy for manufacturing a transfer mask at least includes a thin film for forming a transfer pattern on a substrate. The thin film of the mask blank is generally formed by a film forming apparatus using a sputtering method. Patent Document 1 discloses a DC magnetron sputtering apparatus used to manufacture a mask blank. The sputtering apparatus includes a sputtering target and a substrate holder positioned within a vacuum chamber. The sputtering apparatus also includes a shield, which is a removable component for preventing film adhesion, on the inner wall side of the vacuum chamber.

[0004]

As disclosed in Patent Document 2, the shield of the sputtering apparatus (film forming apparatus) has a structure including a plurality of members combined with each other, and prevents sputtering particles from adhering to the inner wall of the vacuum chamber. Further, labyrinth-shaped vent paths are provided at connecting portions of the plurality of shield members. With the vent paths, an inert gas (such as argon) and a reactive gas (such as oxygen or nitrogen) flowing from the outside into a processing chamber can enter an interior space surrounded by the shield.

## Prior Art Documents

### Patent Documents

[0005]

Patent Document 1: Japanese Patent Application Publication 2005-200682

Patent Document 2: International Publication WO 2010/061603

## Summary of the Invention

### Problems to be Solved by the Invention

[0006]

When the step of forming the thin film on the substrate using the film forming apparatus by the sputtering method as described above (hereinafter referred to as a thin film forming step) is repeated, sputtering particles from the target are deposited on an inner wall of the shield while incorporating the reactive gas. That is, an adhesion film, which has the same constituent elements as the thin film formed on the transparent substrate, is formed on the inner wall of the shield, and a thickness of the adhesion film gradually increases. The adhesion film itself has relatively strong internal stress. As the thickness of the adhesion film increases, the force (tensile force or compressive force) exerted on the adhesion film due to the internal stress increases. When it becomes impossible for the adhesion film to resist the force, the adhesion film cracks and peels off the shield. A portion of the peeled-off adhesion film adheres to the thin film that is being formed on the substrate, and then becomes a factor causing a defect. Thus, the shield is generally exchanged upon reaching a predetermined film formation cycle.

[0007]

The shield of the film forming apparatus is generally made of a metallic material that is hard to be charged, such as aluminum. Further, in a new shield immediately after the exchange, or a new shield immediately after introducing a new film forming apparatus, the metallic material of the shield surface is exposed. When the thin film forming step is performed while in this shield surface state, some sputtering particles, etc. collide with the shield surface, and as a result, metal atoms of the shield may be flicked away and incorporated into a material constituting a thin film for pattern formation to be formed on the substrate. Therefore, before the thin film forming step, steps (aging steps) are conducted which form deposited films by flying particles out of the target through the sputtering method and adhering the particles to a surface on the interior space side of the new shield (hereinafter referred to as a shield inner wall surface).

[0008]

The aging steps are often conducted not only for coating the shield inner wall surface but also for bringing the surface state of the target close to the surface state at the thin film forming step. In this case, in the first aging step, only a noble gas (such as argon) with high sputtering efficiency is introduced into a film forming chamber to cause plasma of the noble gas to collide with the target surface to flick

away each atom constituting the target surface, thereby cleaning the target surface. At this time, most of the atoms flying out of the target surface are deposited on the shield inner wall surface to form a lowermost deposited film.

[0009]

In the next aging step, reactive sputtering is performed under the film forming condition (respective flow rates of the noble gas and reactive gas flowing into the film forming chamber, internal pressure, and voltage applied to the target, etc.) which is almost the same as the condition in the thin film forming step. By this aging step, a deposited film, which has almost the same composition as the thin film for pattern formation to be formed on the substrate in the thin film forming step, is formed on the lowermost deposited film on the shield inner wall surface while the surface state of the target is kept almost the same as that in the thin film forming step.

[0010]

With the film forming apparatus started up through the above aging steps, even if one substrate is placed on a substrate stage and the thin film forming step for forming the thin film for pattern formation on the substrate by the reactive sputtering method is repeated, the variation in physical property such as composition or optical property can be reduced between the thin film for pattern formation formed first on the substrate and the thin film(s) for pattern formation subsequently formed on the substrate.

[0011]

Conventionally, if the thin film forming step is initiated in the film forming apparatus after the aging steps, as the number of manufactured substrates having the thin films for pattern formation increases, a defect rate for the thin films for pattern formation tends to increase. Thus, for every formation of the predetermined number of such substrates, the shield exchange and the aging steps have been conducted to start up the film forming apparatus. However, it was found that depending on the film forming condition for the thin film for pattern formation formed by the film forming apparatus in the thin film forming step, the defect rate for the thin films for pattern formation becomes high upon manufacture of a few such substrates. This problem cannot be solved only by hastening the time of exchange of the shields. It was found that this problem is remarkable especially when the film forming apparatus forms the thin film for pattern formation having indentation hardness of less than 5000MPa in accordance with a nanoindentation method, as detailed below.

[0012]

The present invention was made to solve the above existing problems. It is an object of the present invention to provide a method for starting up a film forming apparatus, wherein even if a thin film for pattern formation, which is made of a material containing a transition metal, silicon, and elements derived from a

reactive gas and has indentation hardness of less than 5000MPa in accordance with a nanoindentation method, is formed on a substrate by a sputtering method using the film forming apparatus started up by the starting-up method, the number of defects detected in the thin film for pattern formation can be significantly reduced.

[0013]

It is also an object of the present invention to provide a method for manufacturing a mask blank, wherein even if a thin film for pattern formation, which is made of a material containing a transition metal, silicon, and elements derived from a reactive gas and has indentation hardness of less than 5000MPa in accordance with a nanoindentation method, is formed on a substrate by a sputtering method using a film forming apparatus so as to manufacture a mask blank, the number of defects detected in the thin film for pattern formation can be significantly reduced. Further, it is also an object of the present invention to provide a method for manufacturing a transfer mask using the mask blank. It is also an object of the present invention to provide a method for manufacturing a semiconductor device using the transfer mask.

#### Means for Solving Problems

[0014]

The present invention includes the following configurations in order to accomplish the above tasks.

(Configuration 1)

A method for starting up a film forming apparatus including a target made of a material containing a transition metal and silicon and a shield in a film forming chamber, characterized in that the method comprises the steps of:

introducing a noble gas and a reactive gas into the film forming chamber and forming a lower layer film on a surface of the shield by reactive sputtering, wherein the lower layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of 5000MPa or more in accordance with a nanoindentation method; and

introducing a noble gas and a reactive gas into the film forming chamber and forming an upper layer film on the lower layer film on the shield by reactive sputtering, wherein the upper layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

[0015]

(Configuration 2)

The method for starting up a film forming apparatus according to Configuration 1, characterized in that the noble gas is a mixed gas of helium and one or more gases selected from argon, krypton, and xenon.

[0016]

(Configuration 3)

The method for starting up a film forming apparatus according to Configuration 2, characterized in that a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the lower layer film is greater than a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the upper layer film.

[0017]

(Configuration 4)

The method for starting up a film forming apparatus according to any one of Configurations 1 to 3, characterized in that the reactive gas in the step of forming the lower layer film and the step of forming the upper layer film at least includes a gas containing nitrogen.

[0018]

(Configuration 5)

The method for starting up a film forming apparatus according to any one of Configurations 1 to 4, characterized in that a ratio of the content of the transition metal divided by the total content of the transition metal and silicon in the target is less than 34%.

[0019]

(Configuration 6)

A method for manufacturing a mask blank using the film forming apparatus started up by the method for starting up a film forming apparatus according to any one of Configurations 1 to 5, characterized in that:

the mask blank includes at least a thin film for pattern formation on a substrate; and

the method comprises the step of:

placing the substrate on a substrate stage provided in the started-up film forming apparatus, introducing a noble gas and a reactive gas into the film forming chamber, and forming the thin film for pattern formation on a main surface of the substrate by reactive sputtering, wherein the thin film for pattern formation is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

[0020]

(Configuration 7)

A method for manufacturing a mask blank using a film forming apparatus including a target made of a material containing a transition metal and silicon, a shield, and a substrate stage in a film forming chamber, characterized in that:

the mask blank includes at least a thin film for pattern formation on a substrate; and

the method comprises the steps of:

introducing a noble gas and a reactive gas into the film forming chamber and forming a lower layer film on a surface of the shield by reactive sputtering, wherein the lower layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of 5000MPa or more in accordance with a nanoindentation method; and

placing the substrate on the substrate stage in the film forming chamber, introducing a noble gas and a reactive gas into the film forming chamber, and forming the thin film for pattern formation on a main surface of the substrate by reactive sputtering, wherein the thin film for pattern formation is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

[0021]

(Configuration 8)

The method for manufacturing a mask blank according to Configuration 7, characterized in that during the step of forming the thin film for pattern formation, a deposited film made of the same material as the material constituting the thin film for pattern formation is also formed on the lower layer film on the shield.

[0022]

(Configuration 9)

The method for manufacturing a mask blank according to Configuration 7 or 8, characterized in that the noble gas is a mixed gas of helium and one or more gases selected from argon, krypton, and xenon.

[0023]

(Configuration 10)

The method for manufacturing a mask blank according to Configuration 9, characterized in that a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the lower layer film is greater than a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the thin film for pattern formation.

[0024]

(Configuration 11)

The method for manufacturing a mask blank according to any one of Configurations 7 to 10, characterized in that the reactive gas in the step of forming the lower layer film and the step of forming the thin film for pattern formation at least includes a gas containing nitrogen.

[0025]

(Configuration 12)

The method for manufacturing a mask blank according to any one of Configurations 7 to 11, characterized in that a ratio of the content of the transition metal divided by the total content of the transition metal and silicon in the target is less than 34%.

[0026]

(Configuration 13)

A method for manufacturing a transfer mask, characterized in that the method comprises the step of using the mask blank manufactured by the method for manufacturing a mask blank according to any one of Configurations 6 to 12 to form a transfer pattern in the thin film for pattern formation by dry etching.

[0027]

(Configuration 14)

A method for manufacturing a semiconductor device, characterized in that the method comprises the step of using the transfer mask manufactured by the method for manufacturing a transfer mask according to Configuration 13 to transfer the transfer pattern to a resist film on a semiconductor substrate by exposure.

Effect of the Invention

[0028]

According to the method for starting up a film forming apparatus of the present invention, even if a thin film for pattern formation, which is made of a material containing a transition metal, silicon, and elements derived from a reactive gas and has indentation hardness of less than 5000MPa in accordance with a nanoindentation method, is formed on a substrate by a sputtering method using the film forming apparatus started up by the starting-up method, the number of defects detected in the thin film for pattern formation can be significantly reduced. Also, according to the method for manufacturing a mask blank of the present invention, even if a thin film for pattern formation, which is made of a material containing a transition metal, silicon, and elements derived from a reactive gas and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method, is formed on the substrate by the sputtering method using the film forming apparatus so as to manufacture the mask blank, the number of defects detected in the thin film for pattern formation can be significantly reduced.

Brief Description of the Drawings

[0029]

Fig. 1 is a schematic view showing one example of a film forming apparatus according to an embodiment of the present invention.

Fig. 2 is a graph showing a relationship between a flow rate of a nitrogen gas during sputtering and the indentation hardness of the formed thin film in Example.

Fig. 3 is a graph showing a relationship between the flow rate of the nitrogen gas during sputtering and the Young's modulus of the formed thin film in Example.

Fig. 4 is a graph showing a relationship between a flow rate of a helium gas during sputtering and the indentation hardness of the formed thin film in Example.

Fig. 5 is a graph showing a relationship between the flow rate of the helium gas during sputtering and the Young's modulus of the formed thin film in Example.

[0030]

While embodiments of the present invention are described below, the circumstances leading to the present invention will be described first. In a manufacturing process of a mask blank, a thin film for pattern formation containing a transition metal, silicon, and elements derived from a reactive gas such as nitrogen has been formed on a substrate by reactive sputtering using a film forming apparatus. For the thin film for pattern formation of the mask blank, the condition of various properties such as a required optical property or etching property changes depending on the condition of properties required for a transfer mask manufactured from the mask blank. The condition of the reactive sputtering in forming the thin film for pattern formation on the substrate by the film forming apparatus (film forming condition) also changes depending on various properties required for the thin film for pattern formation.

[0031]

On the other hand, depending on a grade such as accuracy required for the transfer mask manufactured from the mask blank, the size or number of defects allowed in the thin film for pattern formation of the mask blank varies. There are various factors for causing a defect in the thin film for pattern formation. During formation of the thin film by the reactive sputtering using the film forming apparatus, an adhesion film often falls off a shield inner wall surface to adhere to the thin film, thereby developing a defect. If the thin film is made of a material containing a transition metal, silicon, and elements derived from a reactive gas such as nitrogen (hereinafter also referred to simply as a transition metal silicide compound material) by a sputtering method, a defect due to the adhesion film falling off the shield inner wall surface tends to be easily developed.

[0032]

Then, inspection was attempted for tendencies of the film forming condition in making the thin film of the transition metal silicide compound material by the reactive sputtering and the number of defects detected in the formed thin film. However, there are various fluctuating parameters for the film forming condition in making the thin film of the transition metal silicide compound material by the reactive sputtering. The fluctuating parameters just related to a film forming gas at least include the types, number, and respective introduction flow rates of noble gases introduced into the film forming chamber, the types, number, and respective introduction flow rates of reactive gases introduced into the film forming chamber, a gas pressure within the film forming chamber, and the like. In addition, there are also fluctuating parameters of voltage or current applied to a target (cathode). Moreover, if the thin film of the transition metal silicide compound material is formed by the reactive sputtering, a mixed target of a transition metal and silicon is

used, and thus, there is also a fluctuating parameter of a mixing ratio of the transition metal and silicon in the target material. Therefore, while the individual film forming condition in forming each thin film of the transition metal silicide compound material with a tendency to develop many defects was able to be collected, it was difficult to grasp an overall trend only from the film forming condition.

[0033]

Thus, physical property values of the thin film of the transition metal silicide compound material formed on the substrate by the reactive sputtering were measured to verify whether there was a correlation between the physical property values of the thin film and the number of defects detected in the thin film. As a result, it was found that there was an obvious correlation between the indentation hardness of the thin film in accordance with a nanoindentation method (hereinafter also referred to simply as indentation hardness) and the number of defects detected in the thin film. Specifically, it was found that if the indentation hardness of the thin film was less than 5000MPa, the number of defects detected in the thin film tended to be significantly large. The indentation hardness of the thin film formed on the substrate can be regarded as substantially equal to the indentation hardness of a film adhered to the shield inner wall surface when forming the thin film by the reactive sputtering.

[0034]

The correlation between the indentation hardness of the film adhered to the shield inner wall surface upon the reactive sputtering by the film forming apparatus and the number of defects in the thin film formed on the substrate may be due to a mechanism of defect generation as below. Generally, the metallic material such as aluminum is used as the shield material. During the reactive sputtering by the film forming apparatus, plasma is generated in the internal region surrounded by the shield. At this time, the temperature of the shield increases, and the shield is thermally expanded correspondingly. The adhesion film of the transition metal silicide compound material adhered to the shield inner wall surface also increases in temperature, and is thermally expanded. However, the temperature of the shield decreases while the plasma is not being generated within the film forming chamber. The coefficient of thermal expansion of the transition metal silicide compound material is significantly smaller than that of the metallic material such as aluminum. Thus, a relatively large difference is found between the shield and adhesion film in terms of an expansion and contraction difference upon increase and decrease in the shield temperature. The thin film of the transition metal silicide compound material tends to be poor in malleability relative to the thin film of the metallic material.

[0035]

Due to these factors, when the shield temperature increases and decreases, the adhesion film of the transition metal silicide compound material adhered to the

shield inner wall surface receives the tensile force and compressive force resulting from the expansion and contraction difference from the shield, and then, the adhesion film cannot resist the tensile force and compressive force and causes brittle fracture, resulting in dust emission. Also, the adhesion force between the shield and adhesion film cannot resist the tensile force and compressive force, and a portion of the adhesion film falls off the shield. The substance resulting from the dust emission from the adhesion film or the fallen portion of the adhesion film adheres to a surface of the substrate set on the substrate stage or to a surface of the thin film formed on the substrate, thereby developing into a defect in the thin film.

[0036]

When the thin film formed on the substrate by the film forming apparatus has the indentation hardness of 5000MPa or more, the indentation hardness of the adhesion film adhered to the shield inner wall surface is 5000MPa or more even if the conventional aging steps are applied, and thus, frequency of occurrence of dust emission from the adhesion film or falling of the adhesion film can be kept low. However, if the thin film formed on the substrate by the film forming apparatus has the indentation hardness of less than 5000MPa and the conventional aging steps are applied, the indentation hardness of the adhesion film adhered to the shield inner wall surface is also less than 5000MPa, and thus, it is difficult to avoid frequent occurrence of dust emission from the adhesion film or falling of the adhesion film.

[0037]

[Embodiment 1]

In view of the above, the inventors have reached a conclusion that if the thin film having the indentation hardness of less than 5000MPa is to be formed on the substrate through the sputtering method by the film forming apparatus, the aging steps carried out in the following two steps may be useful in a method for starting up a film forming apparatus. That is, Embodiment 1 of the present invention is a method for starting up a film forming apparatus including a target made of a material containing a transition metal and silicon and a shield within a film forming chamber, characterized in that the method comprises the steps of: introducing a noble gas and a reactive gas into the film forming chamber and forming a lower layer film on a shield inner wall surface by reactive sputtering, wherein the lower layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of 5000MPa or more in accordance with a nanoindentation method; and introducing a noble gas and a reactive gas into the film forming chamber and forming an upper layer film on the lower layer film formed on the shield inner wall surface by reactive sputtering, wherein the upper layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

[0038]

By adhering the lower layer film having the indentation hardness of 5000MPa or more first to the shield inner wall surface, it is possible to improve

durability to the tensile force and compressive force exerted on the lower layer film due to the expansion and contraction difference from the shield associated with the change in temperature, and thus, the falling or brittle fracture of the lower layer film can be controlled. Even after the upper layer film having the indentation hardness of less than 5000MPa is adhered to the lower layer film, the lower layer film directly receives the tensile force and compressive force caused by the expansion and contraction difference from the shield, thereby reducing the tensile force and compressive force exerted on the upper layer film. The lower layer film and upper layer film are made of the materials containing the same transition metal and silicon. Thus, the lower layer film and upper layer film are chemically bonded at their interface, and the adhesion force between the lower layer film and upper layer film is significantly higher than the adhesion force in direct adhesion of the upper layer film to the shield inner wall surface. These factors compositely interacting with each other can significantly suppress the falling or brittle fracture of the upper layer film.

[0039]

The constitution of the present invention above is described below in detail. Fig. 1 is a schematic view of a film forming apparatus according to Embodiment 1 of the present invention. The film forming apparatus 1 is for forming a thin film for pattern formation on a main surface of a substrate 100 by reactive sputtering. The film forming apparatus 1 includes a film forming chamber 2, a substrate stage 3, a cathode 4, a gas inflow section 5, a gas discharging section 6, a lower shield 71, and an upper shield 72 (the lower shield 71 and upper shield 72 are hereinafter collectively also referred to as a shield 7). The substrate stage 3 on which the substrate 100 is to be placed is provided with its rotary shaft 31 extending through a lower wall of the film forming chamber 2. The cathode 4 is provided to extend through an upper wall of the film forming chamber 2. A target 9 is attached to the cathode 4 with a backing plate 8 therebetween. The shield 7 is provided such that sputtering particles flying out of the target 9 are prevented from adhering to the inner wall surface of the film forming chamber 2 during the sputtering by the film forming apparatus 1.

[0040]

A film forming gas, i.e., a mixed gas of a noble gas and a reactive gas, is introduced from the gas inflow section 5 into the film forming chamber 2. Then, the film forming gas in the film forming chamber 2 is discharged from the gas discharging section 6. The gas discharging section 6 is also used to evacuate the film forming chamber 2 to a predetermined degree of vacuum. A plurality of gas inflow sections 5 may be provided in the film forming chamber 2. For example, the inflow section for noble gas inflow and the inflow section for reactive gas inflow, i.e., two gas inflow sections 5, may be provided in the film forming chamber 2, or alternatively, inflow sections for respective types of gases may be provided in the film forming chamber 2.

[0041]

The cross section of each tip (junction) of the lower shield 71 and upper shield 72 has a concave shaped portion. The lower shield 71 and upper shield 72 engage with each other and are placed within the film forming chamber 2 such that a space is left between their concave shaped portions. Such a structure with the space being left is referred to as a labyrinth structure. The film forming gas flows in and out between an inner region surrounded by respective inner wall surfaces of the lower shield 71 and upper shield 72 in the film forming chamber 2 (hereinafter referred to as a shield interior region) and a region outside of the lower shield 71 and upper shield 72 in the film forming chamber 2 (hereinafter referred to as a shield exterior region) through the labyrinth structure. The shield 7 is preferably made of a material in which the metal content is highest among elements constituting the material, and more preferably made of a metallic material. The shield 7 is further preferably made of aluminum, iron, copper, etc.

[0042]

The inner wall surface of the shield 7 preferably receives sandblast treatment, etc. to have predetermined surface roughness (minute unevenness). With the inner wall surface of the shield 7 having the predetermined surface roughness, it is expected that the adhesion force of the lower layer film (or a lowermost layer film, if the lowermost layer film is formed between the shield 7 and lower layer film, as described below), which is directly adhered to the inner wall surface, with respect to the shield 7 is improved by an anchor effect. For example, the predetermined surface roughness is preferably  $5\mu\text{m}$  or more, and more preferably  $6\mu\text{m}$  or more, in arithmetic mean estimation  $R_a$ .

[0043]

The cathode 4 may be used in both DC power system and RF power system. That is, the method for starting up a film forming apparatus according to Embodiment 1 is applicable to both a film forming apparatus of DC sputtering system and a film forming apparatus of RF sputtering system. In the case of a film forming apparatus of sputtering system such that plasma exists in the shield interior region to cause the relatively great thermal expansion of the shield during aging (sputtering), the application of the method for starting up a film forming apparatus according to Embodiment 1 provides a benefit.

[0044]

The method for starting up a film forming apparatus according to Embodiment 1 is particularly effective if a thin film for pattern formation formed on a main surface of the substrate 100 using the started-up film forming apparatus 1 is made of a material containing a transition metal, silicon, and elements derived from a reactive gas, and has the indentation hardness of less than  $5000\text{MPa}$ . This is because the aging steps in starting up the film forming apparatus 1 require the reactive sputtering under the film forming condition substantially the same as the condition in forming the thin film for pattern formation. In this case, a film adhered to the shield inner wall surface at the aging steps easily causes film separation (falling off the shield) or dust emission due to brittle fracture by thermal

expansion of the shield.

[0045]

The method for starting up a film forming apparatus according to Embodiment 1 is characterized in that the aging steps for introducing a noble gas and a reactive gas into the film forming chamber 2 and applying voltage to a target made of a material containing a transition metal and silicon to cause the reactive sputtering are carried out in at least two steps: the step of forming the lower layer film on the inner wall surface of the shield 7; and the step of forming the upper layer film. The lower layer film formed first on the shield inner wall surface is made of a material containing a transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of 5000MPa or more. The indentation hardness of the lower layer film is more preferably 5500MPa or more, and further preferably 6000MPa or more. This is because the durability to thermal expansion of the shield increases with an increase in indentation hardness of the lower layer film.

[0046]

The indentation hardness used herein refers to hardness measured in accordance with the principle of a nanoindentation method established in ISO 14577. More specifically, a special probe having a diamond indenter is pushed from the surface of the thin film by an atomic force microscope (AFM). The displacement in a depth direction before and after pushing the diamond indenter is measured using an optical displacement detector to measure a change in load. Further, an AFM image of an indentation in the thin film after removing the diamond indenter is obtained, thereby calculating the indentation hardness using the information.

[0047]

The film forming condition used in reactive sputtering for forming the lower layer film is the condition found through the prior experiment with the film forming apparatus to be started up. In the experiment, for example, thin films are formed on respective substrates under various film forming conditions by the film forming apparatus to be started up, and the indentation hardness of the respective thin films is measured to obtain the relationship between the film forming conditions and the indentation hardness of the thin films, thereby selecting the film forming condition for the step of forming the lower layer film.

[0048]

The upper layer film formed on the lower layer film is made of a material containing a transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of less than 5000MPa. The indentation hardness of the upper layer film is more preferably 4500MPa or less, and further preferably 4000MPa or less. This is because the lower indentation hardness the upper layer film has, the greater effect the present invention provides. In the step of forming the upper layer film, the reactive sputtering is performed under the film forming

condition substantially the same as the film forming condition for forming the thin film for pattern formation on the substrate after the film forming apparatus is started up. Generally, the aging steps principally intend to bring the target surface state close to the target surface state during forming the thin film for pattern formation on the substrate by the reactive sputtering after starting up the film forming apparatus. The target surface state upon completing the step of forming the lower layer film is not close to the target surface state during forming the thin film for pattern formation on the substrate.

[0049]

By the step of forming the upper layer film, it is possible to bring the target surface state close to the target surface state during forming the thin film for pattern formation on the substrate, while increasing the durability to the tensile force and compressive force associated with the thermal expansion of the shield by means of the laminated structure of the upper and lower layer films. Since both the lower layer film and upper layer film are formed from sputtering particles flying out of the target made of materials containing the same transition metal and silicon, the lower layer film and upper layer film are made of the materials containing the same transition metal and silicon. In view of the target surface state, the noble gas and reactive gas used in the reactive sputtering for forming the lower layer film are the same as the noble gas and reactive gas used in the reactive sputtering for forming the thin film for pattern formation. Further, a flow rate ratio per unit time of the noble gas and reactive gas in forming the lower layer film by the reactive sputtering is preferably the same as the flow rate ratio per unit time of the noble gas and reactive gas in forming the thin film for pattern formation by the reactive sputtering. The film forming conditions, such as a gas pressure within the film forming chamber and voltage applied to the target, in forming the lower layer film by the reactive sputtering and in forming the thin film for pattern formation by the reactive sputtering are preferably the same.

[0050]

From the points of view of reducing the difference in the target surface state between the lower layer film formation and the upper layer film formation, and of increasing the bonding force between the lower layer film and the upper layer film, at least one reactive gas used in the reactive sputtering for forming the lower layer film is preferably the same in type as at least one reactive gas used in the reactive sputtering for forming the upper layer film. More preferably, all of the reactive gases used in the reactive sputtering for forming the lower layer film are the same in type as all of the reactive gases used in the reactive sputtering for forming the upper layer film.

[0051]

The noble gas used to form the upper layer film and lower layer film is one or more gases selected from helium, neon, argon, krypton, and xenon. In particular, in view of the sputtering efficiency from the target in the reactive sputtering, the noble gas used to form the upper layer film and lower layer film

preferably includes one or more gases selected from argon, krypton, and xenon. If the thin film for pattern formation containing a transition metal, silicon, and elements derived from the reactive gas is formed by the reactive sputtering, the thin film tends to have relatively high film stress. In order to decrease the film stress of the thin film, a helium gas is preferably incorporated into the thin film during the reactive sputtering. By annealing the substrate having such a thin film formed thereon, the helium gas in the thin film is released into the atmosphere to create a minute space within the thin film. Other elements in the thin film move into the minute space during annealing, thereby decreasing the stress of the thin film.

[0052]

In view of the sputtering efficiency in the thin film formation and the decrease in the stress of the thin film, the noble gas used to form the thin film for pattern formation on the substrate is preferably a mixed gas of helium and one or more gases selected from argon, krypton, and xenon. Further, in view of the manufacturing cost, this noble gas is more preferably a mixed gas of argon and helium. Features regarding the film stress of the thin film for pattern formation also apply to the lower layer film and upper layer film adhered to the shield inner wall surface in the aging steps. Thus, the noble gas used to form the lower layer film and upper layer film by the reactive sputtering is also preferably a mixed gas of helium and one or more gases selected from argon, krypton, and xenon. As in the case of the thin film for pattern formation, this noble gas is more preferably a mixed gas of argon and helium.

[0053]

As described below, a mixed gas of an argon gas and a helium gas, and a nitrogen gas were used as the noble gas and the reactive gas flowed into the film forming chamber 2, respectively, so as to make an experiment to conduct the reactive sputtering for forming the thin films on the substrate under the varying film forming conditions. Specifically, while the flow rate per unit time of the argon gas and nitrogen gas was unchanged, the flow rate per unit time of the helium gas was changed. Then, the indentation hardness of each thin film formed was measured. As a result, it was found that as the flow rate per unit time of helium was increased, the indentation hardness of the thin film formed under the corresponding film forming condition tended to increase.

[0054]

In view of the above result, a ratio of the flow rate per unit time of the helium gas in the noble gas introduced into the film forming chamber 2 divided by the total flow rate per unit time of the noble gas in the step of forming the lower layer film is preferably greater than a ratio of the flow rate per unit time of the helium gas in the noble gas introduced into the film forming chamber 2 divided by the total flow rate per unit time of the noble gas in the step of forming the upper layer film. In this way, it is possible to provide the lower layer film with the indentation hardness of 5000MPa or more and the upper layer film with the indentation hardness of less than 5000MPa while the same elements are used to

constitute the lower layer film and upper layer film, respectively.

[0055]

A gas containing at least one of nitrogen, oxygen, carbon, and hydrogen is applicable as the reactive gas used to form the upper layer film and lower layer film. The thin film for pattern formation formed on the substrate using the film forming apparatus 1 often contains nitrogen as an element derived from the reactive gas. As the nitrogen content in the thin film increases, a refractive index  $n$  tends to increase while an extinction coefficient  $k$  tends to decrease. The thin film having such an optical property is suitable for a halftone phase shift film. On the other hand, in the manufacture of a transfer mask from a mask blank having the thin film for pattern formation of the transition metal silicide-based material, a black defect in a thin film pattern is corrected by electron beam irradiation and the supply of a fluorine-based gas (such as  $\text{XeF}_2$ ) in an unexcited state (correction of EB defect). The thin film of the transition metal silicide-based material, if it contains a small amount of oxygen or nitrogen, is easily etched even if it is exposed to  $\text{XeF}_2$  with no electron beam being irradiated. In view of this, nitrogen in a predetermined amount or more has been contained in a light-shielding film of the transition metal silicide-based material.

[0056]

Because of this situation, a gas containing nitrogen is often used as the reactive gas in the reactive sputtering for making the thin film for pattern formation of the transition metal silicide-based material. Thus, it would be preferable that the reactive gas in the steps of forming the lower layer film and forming the upper layer film as the aging steps for the film forming apparatus 1 at least includes the gas containing nitrogen. Such a reactive gas may include, for example,  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$ , and the like.

[0057]

The target 9 is made of a material containing a transition metal and silicon. This is because the material containing elements derived from the reactive gas in addition to a transition metal and silicon easily causes brittle fracture due to insufficient malleability relative to a metal-based material, and thus, the method for starting up a film forming apparatus according to Embodiment 1 provides the great effect. This is also because the thin film of the transition metal silicide-based material is suitable as a material of a light-shielding film or halftone phase shift film. As for the transition metal silicide-based material used for the thin film for pattern formation, a conventionally widely used transition metal element is molybdenum (Mo), but the transition metal element is not limited thereto. The transition metal element may include any one or more metallic elements of tantalum (Ta), tungsten (W), titanium (Ti), chromium (Cr), hafnium (Hf), nickel (Ni), vanadium (V), zirconium (Zr), ruthenium (Ru), rhodium (Rh), zinc (Zn), niobium (Nb), and palladium (Pd).

[0058]

A ratio [%] of the content [at%] of the transition metal (M) divided by the total content [at%] of the transition metal (M) and silicon (Si) (hereinafter referred to as "M/[M+Si] ratio") in the thin film for pattern formation formed using the target 9 is close to the value of the M/[M+Si] ratio of the target 9. To the extent of the M/[M+Si] ratio up to about 34%, around which the M/[M+Si] ratio is stoichiometrically stable ( $\text{MoSi}_2$  for a molybdenum silicide; many other transition metal silicides show a similar tendency), the thin film of the transition metal silicide-based material tends to increase in optical density with respect to ArF exposure light with the increase in M/[M+Si] ratio. It also tends to decrease in optical density as the M/[M+Si] ratio becomes further higher than about 34%.

[0059]

The thin film of the transition metal silicide-based material decreases in light fastness with respect to the ArF exposure light as the M/[M+Si] ratio increases. In view of this, the M/[M+Si] ratio in the target 9 is preferably less than 34%, more preferably 25% or less, and further preferably 20% or less. In view of conductivity, etc. of the target 9 or thin film for pattern formation, the M/[M+Si] ratio of the target 9 is preferably 1% or more, and more preferably 2% or more.

[0060]

The method for starting up a film forming apparatus according to Embodiment 1 also includes an aspect in which the step of forming a lowermost layer film is conducted before the step of forming the lower layer film on the shield inner wall surface. That is, the lower layer film of the present invention includes not only the lower layer film directly formed on a surface of the shield 7, but also the lower layer film formed on the surface of the shield 7 with the lowermost layer film interposed therebetween. Specifically, in the step of forming a lowermost layer film, only a noble gas is introduced into the film forming chamber 2 to cause sputtering to make the lowermost layer film of a material substantially made of a transition metal and silicon on the surface of the shield 7 (shield inner wall surface). The material substantially made of a transition metal and silicon, which forms the lowermost layer film, is a material made of only a transition metal and silicon, as well as a material in which a trace of an element inevitably incorporated into the lowermost layer film during sputtering (noble gas, and elements resulting in contamination, such as water) is mixed.

[0061]

When the shield 7 in the film forming apparatus 1 is exchanged, the interior of the film forming chamber 2 is open to the atmosphere. The target 9 is also open to the atmosphere, and thus, it is difficult to avoid the formation of an oxide film on a surface of the target 9. After the shield 7 is exchanged, the aging steps for starting up the film forming apparatus 1 are performed. However, if the step of forming the lower layer film by the reactive sputtering with a film forming gas including a reactive gas is performed first, abnormal discharge may occur depending on an oxidation state of the surface of the target 9. The abnormal discharge causes dust emission from the target 9 or deterioration of the surface state of the target 9.

[0062]

In view of this, it is preferable to cause the sputtering by introducing only a noble gas into the film forming chamber 2 and applying voltage to the target 9 before conducting the step of forming the lower layer film of the aging steps. Only particles of the noble gas collide with the surface of the target 9 to flick away constituent elements on the surface of the target 9, such that a surface layer including the oxide film of the target 9 may be removed. Respective particles of the transition metal and silicon flying out of the target 9 adhere to the inner wall surface of the shield 7 to form the lowermost layer. Most of the oxygen flicked away from the target 9 does not adhere to the shield 7, and is discharged along with the noble gas outside the system from the gas discharging section 6. Thus, the lowermost layer film adhered to the inner wall surface of the shield 7 is made of the material substantially made of a transition metal and silicon.

[0063]

The lowermost layer film formed on the shield inner wall surface is made of a material not containing elements derived from the reactive gas. The lowermost layer film made of such a material has the indentation hardness similar to the upper layer film, but it has a significantly lower Young's modulus than the upper layer film, and is easily elastically deformed. That is, the lowermost layer film causes less brittle fracture upon thermal expansion of the shield 7 relative to the upper layer film. Since both the lowermost layer film and lower layer film are made of the materials containing the same transition metal and silicon, chemical bonding force at their interface is relatively strong. With these actions, even if the adhesion film which includes the lowermost layer film, lower layer film, and upper layer film deposited in said order is formed on the inner wall surface of the shield 7, dust emission or falling of the adhesion film associated with the thermal expansion of the shield 7 may be reduced.

[0064]

The step of forming the lowermost layer film is performed for the main purpose of approximating the surface of the target 9 to the state wherein it contains only target's constituent elements. Thus, any one gas of argon, krypton, and xenon having relatively high atomic weight or a mixed gas of two or more gases selected therefrom is preferably used as the noble gas introduced into the film forming chamber 2.

[0065]

Embodiment 1 also provides a method for manufacturing a mask blank using the film forming apparatus started up by the above-described method for starting up a film forming apparatus. Specifically, it is a method for manufacturing a mask blank including at least a thin film for pattern formation on a substrate, characterized in that the method comprises the step of: placing the substrate 100 on the substrate stage 3 provided in the film forming apparatus 1 started up by the above method for starting up a film forming apparatus, introducing a noble gas and a

reactive gas, and forming the thin film for pattern formation on a main surface of the substrate 100 by the reactive sputtering, wherein the thin film for pattern formation is made of a material containing a transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

[0066]

The film forming condition in the step of forming the thin film for pattern formation on the substrate 100 is substantially the same as the film forming condition in the step of forming the upper layer film on the inner wall surface of the shield 7. During the step of forming the thin film for pattern formation, an adhesion film which has constituent elements and a physical property substantially the same as the thin film for pattern formation is newly formed on the upper layer film. However, since the newly formed adhesion film has the constituent elements and composition substantially the same as the upper layer film, there is high bonding force between the upper layer film and adhesion film. Therefore, it is hard for the newly formed adhesion film to fall off the upper layer film.

[0067]

The mask blank manufactured using this method for manufacturing a mask blank at least includes, on the substrate 100, the thin film for pattern formation which is made of a material containing a transition metal, silicon, and elements derived from a reactive gas and has the indentation hardness of less than 5000MPa in accordance with the nanoindentation method. The thin film for pattern formation is a thin film in which a transfer pattern is to be formed by etching when manufacturing a transfer mask from the mask blank. The thin film for pattern formation includes one for remaining as a thin film having the transfer pattern in the finally completed transfer mask, as well as one for temporarily existing as a hard mask film having the transfer pattern during manufacturing the transfer mask from the mask blank. The thin film for pattern formation is used in, for example, a light-shielding film, a phase shift film, a hard mask film, an etching stopper film, and the like.

[0068]

If the transfer mask manufactured from the mask blank is a binary mask, the mask blank has a constitution wherein a light-shielding film is provided on the substrate 100, or a constitution wherein a hard mask film is laminated on the light-shielding film. If the transfer mask manufactured from the mask blank is a halftone phase shift mask, the mask blank has a constitution wherein a phase shift film and a light-shielding film are provided on the substrate 100, or a constitution wherein a hard mask film is laminated on the light-shielding film. Further, a mask blank including an etching stopper film between the substrate 100 and the phase shift film, and a mask blank including an etching stopper film between the phase shift film and the light-shielding film are also included.

[0069]

When the transfer mask manufactured from the mask blank is used in an exposure apparatus, the exposure light is preferably, but not limited to, the ArF exposure light (wavelength: 193nm) from an ArF excimer laser as a light source. The mask blank manufactured using this method for manufacturing a mask blank is also applicable as a mask blank for manufacturing a transfer mask used in the exposure apparatus using KrF exposure light (wavelength: 248nm) or i-line exposure light (wavelength: 365nm).

[0070]

When the thin film for pattern formation is a light-shielding film for forming a light-shielding pattern in a binary mask, the light-shielding film should have optical density (OD) of at least 2.0 or more with respect to the exposure light, and the optical density is more preferably 2.5 or more, and further preferably 2.8 or more. When the thin film for pattern formation is a light-shielding film for forming a pattern including a light-shielding band in a halftone phase shift mask, the light-shielding film should have optical density (OD) of at least 2.0 or more with respect to the exposure light in the laminated structure of the light-shielding film and phase shift film, and the optical density is more preferably 2.5 or more, and further preferably 2.8 or more.

[0071]

When the thin film for pattern formation is a phase shift film for forming a phase shift pattern in a halftone phase shift mask, the phase shift film is preferably regulated such that the transmittance with respect to the exposure light is not less than 1% and not more than 30% and such that a phase difference between the ArF exposure light transmitted through the phase shift film and the light traveling through air for the same distance as the thickness of the phase shift film is not less than 150 degrees and not more than 190 degrees.

[0072]

The thin film for pattern formation may be a single layer structure, or a laminated structure comprised of two or more layers. Respective layers in the thin film for pattern formation of the single layer structure and of the laminated structure comprised of two or more layers may include a configuration having substantially the same composition in a thickness direction of the film or layer, or a configuration with a compositional gradient in the thickness direction of the layer. In either configuration of the thin film for pattern formation, the thin film formed first on the substrate 100 by the reactive sputtering using the film forming apparatus 1 started up by the method according to Embodiment 1 should have the indentation hardness of less than 5000MPa. The thin film formed first is more preferably formed under the film forming condition substantially the same as the condition in forming the upper layer film on the shield 7 (that is, the thin film formed first has substantially the same composition as the upper layer film). This is because the thin film formed first is a film that first adheres to the upper layer film on the shield 7.

[0073]

The substrate 100 is preferably a transparent substrate that is transparent to the exposure light. The substrate 100 is also preferably made of a glass material. The substrate 100 can be made of synthetic quartz glass, quartz glass, aluminosilicate glass, soda lime glass, low thermal expansion glass ( $\text{SiO}_2$ - $\text{TiO}_2$  glass, etc.), and the like. Among these, synthetic quartz glass is especially preferable as a material for forming the substrate of the mask blank since it has high transmittance with respect to the ArF exposure light and also has sufficient stiffness to cause less deformation.

[0074]

With reference to Fig. 1, the positional relationship between the substrate 100 and target 9 in forming the thin film for pattern formation is described. An offset distance Doff (distance between a central axis 21 of the substrate 100 and a straight line 22 extending through the center of the target 9 and parallel to the central axis 21 of the substrate 100) can be regulated by an area in which in-plane uniformity in film thickness of the thin film for pattern formation should be ensured. Generally, if the area in which good in-plane uniformity should be ensured is large, the required offset distance Doff is large. For example, when the substrate 100 is a quadrangle 152mm on a side, the region of the thin film where the transfer pattern is formed is generally an inner region within a quadrangle 132mm on a side based on the center of the substrate 100. In order for film thickness distribution of the thin film to achieve accuracy within  $\pm 1\text{nm}$  in the inner region within the quadrangle 132mm on a side, the offset distance Doff should be between approximately 240mm and 400mm, and the preferable offset distance Doff is between 300mm and 380mm.

[0075]

The optimal range of a vertical distance (H) between the target 9 and substrate 100 changes depending on the offset distance Doff. For example, in order to ensure good in-plane uniformity within the substrate 100 that is a quadrangle 152mm on a side, the vertical distance (H) between the target 9 and substrate 100 should be between approximately 200mm and 380mm, and the preferable distance (H) is between 210mm and 300mm. A target tilt angle  $\theta$  has an influence not only on the in-plane uniformity in film thickness of the thin film but also on a deposition rate of the thin film. Specifically, in order to obtain good in-plane uniformity in film thickness of the thin film and a high deposition rate, the target tilt angle  $\theta$  is preferably between 10 degrees and 30 degrees.

[0076]

[Embodiment 2]

The present invention includes Embodiment 2, in which, regarding the aging steps for the film forming apparatus 1, the step of forming the upper layer film is omitted after completing the step of forming the lower layer film on the inner wall surface of the shield 7, and the thin film for pattern formation is then formed on the substrate 100 using the film forming apparatus 1 to manufacture the mask blank. That is, the method for manufacturing a mask blank according to Embodiment 2 is a method for manufacturing a mask blank using the film forming apparatus 1 including

the target 9 made of a material containing a transition metal and silicon, the shield 7, and the substrate stage 3 within the film forming chamber 2, characterized in that the mask blank includes at least the thin film for pattern formation on the substrate 100, and the method comprises the steps of: introducing a noble gas and a reactive gas into the film forming chamber 2 and forming the lower layer film on a surface of the shield 7 by the reactive sputtering, wherein the lower layer film is made of a material containing a transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of 5000MPa or more in accordance with the nanoindentation method; and placing the substrate 100 on the substrate stage 3 within the film forming chamber 2, introducing a noble gas and a reactive gas, and forming the thin film for pattern formation on a main surface of the substrate 100 by the reactive sputtering, wherein the thin film for pattern formation is made of a material containing a transition metal, silicon, and elements derived from the reactive gas, and has the indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

[0077]

Embodiment 2 is especially effective when dust emission such as abnormal discharge is less likely to occur on the surface of the target 9 and uniformity in film thickness distribution or optical property of the thin film for pattern formation formed on the substrate 100 may be increased even if the thin film for pattern formation is formed by the reactive sputtering with the surface state of the target 9 after the step of forming the lower layer film unchanged. Regarding the method for manufacturing a mask blank according to this embodiment, in the step of forming the thin film for pattern formation, a deposited film made of a material the same as the material constituting the thin film for pattern formation is also formed on the lower layer film formed on a surface of the shield 7. Since this deposited film is comprised of the same constituent elements as the lower layer film, the chemical bonding force between the deposited film and the lower layer film is high.

[0078]

Features related to the noble gas with respect to the relationship between the lower layer film and upper layer film of Embodiment 1 also apply to Embodiment 2. In Embodiment 2, the noble gas used to form the lower layer film and thin film for pattern formation is also preferably a mixed gas of helium and one or more gases selected from argon, krypton, and xenon. The ratio of a flow rate per unit time of the helium gas in the noble gas introduced into the film forming chamber divided by the total flow rate per unit time of the noble gas in the step of forming the lower layer film is preferably greater than the ratio of a flow rate per unit time of the helium gas in the noble gas introduced into the film forming chamber divided by the total flow rate per unit time of the noble gas in the step of forming the thin film for pattern formation.

[0079]

Features related to the reactive gas with respect to the relationship between the lower layer film and upper layer film of Embodiment 1 also apply to

Embodiment 2. In Embodiment 2, the reactive gas in the steps of forming the lower layer film and forming the thin film for pattern formation also preferably at least includes a gas containing nitrogen. Features related to the target 9 of Embodiment 1 also apply to Embodiment 2. The  $M/[M+Si]$  ratio in the target is preferably less than 34%. The other features in Embodiment 1 also apply to Embodiment 2, except that Embodiment 2 does not include the step of forming the upper layer film on the lower layer film formed on the inner wall surface of the shield 7.

[0080]

The present invention includes a method for manufacturing a transfer mask, characterized in that the method comprises the step of using the mask blank manufactured by the method for manufacturing a mask blank according to any one of Embodiment 1 and Embodiment 2 to form a transfer pattern in the thin film for pattern formation by dry etching.

[0081]

If the transfer mask is a binary mask, the binary mask is manufactured by, for example, the following manufacturing method. First, the method for manufacturing a mask blank according to Embodiment 1 or Embodiment 2 is used to manufacture a mask blank which includes a light-shielding film (thin film for pattern formation) and a hard mask film laminated on the substrate 100. The hard mask film is preferably made of a material containing chromium. Then, a resist film for electron beam lithography exposure is formed on the hard mask film by a spin coating method. Subsequently, the resist film is subjected to the lithography exposure of the transfer pattern using an electron beam lithography system, and then, a development treatment, etc. is applied, thereby forming a resist pattern.

[0082]

Next, the dry etching with a mixed gas of a chlorine-based gas and an oxygen gas using the resist pattern as a mask is performed to form the transfer pattern in the hard mask film. Then, the dry etching with a fluorine-based gas using the hard mask film having the transfer pattern as a mask is performed to form the transfer pattern in the light-shielding film. Finally, the hard mask film is removed by the dry etching, etc., and a predetermined treatment such as a washing treatment is applied to complete the binary mask. In the above manufacture of the binary mask, the resist film may be directly formed on the light-shielding film after HMDS (hexamethyldisilazane) treatment on a surface of the light-shielding film, without providing the hard mask film in the mask blank.

[0083]

If the transfer mask is a halftone phase shift mask, the halftone phase shift mask is manufactured by, for example, the following manufacturing method. First, the method for manufacturing a mask blank according to Embodiment 1 or Embodiment 2 is used to manufacture a mask blank which includes a phase shift film

(thin film for pattern formation) and a light-shielding film laminated on the substrate 100. The light-shielding film is preferably made of a material containing chromium. Then, a resist film for electron beam lithography exposure is formed on the light-shielding film by a spin coating method. Subsequently, the resist film is subjected to the lithography exposure of the transfer pattern using an electron beam lithography system, and then, the development treatment, etc. is applied, thereby forming a first resist pattern.

[0084]

Next, the dry etching with a mixed gas of a chlorine-based gas and an oxygen gas using the first resist pattern as a mask is performed to form the transfer pattern in the light-shielding film. Then, the dry etching with a fluorine-based gas using the light-shielding film having the transfer pattern as a mask is performed to form the transfer pattern in the phase shift film. After that, a new resist film is formed on the light-shielding film, the resist film is subjected to lithography exposure of a pattern including a light-shielding band, and then, a development treatment, etc. is applied, thereby forming a second resist pattern. Next, the dry etching with a mixed gas of a chlorine-based gas and an oxygen gas using the second resist pattern as a mask is performed to form a pattern including the light-shielding band in the light-shielding film. Finally, a predetermined treatment such as a washing treatment is applied to complete the halftone phase shift mask.

[0085]

In the manufacture of the above halftone phase shift mask, after a hard mask film made of a material containing silicon is provided on the light-shielding film of the mask blank and the HMDS treatment is carried out on the surface of the hard mask film, the resist film may be formed on the hard mask film.

[0086]

The present invention includes a method for manufacturing a semiconductor device, characterized in that the method comprises the step of using the transfer mask manufactured by the above method for manufacturing a transfer mask to transfer the transfer pattern to the resist film on a semiconductor substrate by exposure.

Example

[0087]

Embodiments of the present invention are further specifically described below in association with Example.

(Example and comparative example)

[Starting up of the film forming apparatus]

In this Example, a mask blank for a halftone phase shift mask to which the ArF exposure light is applied is manufactured. The mask blank has a structure in which a phase shift film, a light-shielding film, and a hard mask film are laminated in this order on a synthetic quartz glass substrate 100 (of which main surface has a dimension of about 152mm x about 152mm and a thickness of about 6.35 mm).

Among the laminated films, the phase shift film is a thin film for pattern formation made of a transition metal, silicon, and nitrogen. The phase shift film has such an optical property as transmittance of 6% with respect to the ArF exposure light and a phase difference of 177 degrees.

[0088]

The phase shift film was formed on the substrate 100 using a DC magnetron sputtering type film forming apparatus 1. Specifically, a mixed target 9 of molybdenum (Mo) and silicon (Si) (at% ratio of Mo:Si=4:96) was used, a mixed gas of nitrogen (N<sub>2</sub>), argon (Ar), and helium (He) (flow rate ratio [sccm] of N<sub>2</sub>:Ar:He=18:9:30, pressure =0.3Pa) was introduced from the gas inflow section 5 into the film forming chamber 2, and voltage was applied to the cathode 4 (target 9) at power of 2.4kW to cause the reactive sputtering, thereby forming the phase shift film having a film thickness of 61nm. For the phase shift film formed, an additional function of an atomic force microscope (Dimension Icon: manufactured by Bruker Corporation) was used to measure the indentation hardness of the phase shift film in accordance with the nanoindentation method, and as a result, the indentation hardness was 3145[MPa]. Since this phase shift film has the indentation hardness of less than 5000[MPa], the conventional method for starting up a film forming apparatus will frequently cause film separation or dust emission from the deposited film adhered to the inner wall surface of the shield 7. If the film forming apparatus used to form the phase shift film is started up by the method for starting up a film forming apparatus according to the present invention, defects in the phase shift film can be reduced.

[0089]

In order to use the method for starting up a film forming apparatus according to the present invention, it is necessary to select the film forming condition used in the step of forming the lower layer film on the inner wall surface of the shield 7, i.e., the film forming condition such that the lower layer film having the indentation hardness of 5000MPa or more is formed on the inner wall surface of the shield 7. Then, experiments were made by varying the condition based on the film forming condition for forming the phase shift film by the film forming apparatus 1, thereby selecting the film forming condition for forming the lower layer film. Since the same target 9 was used in the lower layer film formation and in the phase shift film formation, the mixing ratio of molybdenum and silicon could not be changed. Therefore, the thin films were formed on respective substrates while respective flow rates per unit time of the argon gas and helium gas flowed into the film forming chamber 2 were fixed (Ar=9[sccm], He=30[sccm]) and the flow rate per unit time of the nitrogen gas was varied, and then, the indentation hardness and Young's modulus of each thin film were measured in a way similar to the above (the above atomic force microscope could measure the Young's modulus by the additional function).

[0090]

Fig. 2 is a graph showing a relationship between the flow rate [sccm] per

unit time of the nitrogen gas during the reactive sputtering for forming the thin film and the indentation hardness [MPa] of the formed thin film. Fig. 3 is a graph showing a relationship between the flow rate [sccm] per unit time of the nitrogen gas during the reactive sputtering for forming the thin film and the Young's modulus [MPa] of the formed thin film. The graph in Fig. 2 shows that the indentation hardness of the thin film does not significantly change even if the flow rate per unit time of the nitrogen gas is varied, and there is no film forming condition which can realize the indentation hardness of 5000[MPa] or more. The graph in Fig. 3 shows that the Young's modulus of the thin film tends to increase with the increase in flow rate per unit time of the nitrogen gas. It also shows that since the flow rate per unit time of the nitrogen gas correlates with the nitrogen content in the thin film, the Young's modulus of the thin film made of the material containing silicon, molybdenum (transition metal), and nitrogen tends to be higher with the increase in nitrogen content.

[0091]

According to Fig. 2, when the flow rate per unit time of the nitrogen gas is zero (i.e., sputtering is done with the argon gas and helium gas only), the thin film has the lowest Young's modulus. Since the thin film has the low Young's modulus, it causes relatively less brittle fracture when the external force is applied thereto. This film forming condition is substantially the same as the film forming condition in the sputtering for cleaning the target surface with introduction of only the noble gas at the first stage for conventional starting up of a film forming apparatus. Based on this result, even if the lowermost layer film of molybdenum silicide (transition metal silicide) first adheres to the inner wall surface of the shield 7 by the sputtering for cleaning the target surface, the brittle fracture or falling due to the tensile force and compressive force exerted on the lowermost layer film by thermal expansion of the shield 7 would be less likely to occur.

[0092]

Next, the thin films were formed on respective substrates while respective flow rates per unit time of the nitrogen gas and argon gas flowed into the film forming chamber 2 were fixed ( $N_2=18$ [sccm],  $Ar=9$ [sccm]) and the flow rate per unit time of the helium gas was varied, and then, the indentation hardness and Young's modulus of each thin film were measured in a way similar to the above (the above atomic force microscope could measure the Young's modulus by the additional function). Fig. 4 is a graph showing a relationship between the flow rate [sccm] per unit time of the helium gas during the reactive sputtering for forming the thin film and the indentation hardness [MPa] of the formed thin film. Fig. 5 is a graph showing a relationship between the flow rate [sccm] per unit time of the helium gas during the reactive sputtering for forming the thin film and the Young's modulus [MPa] of the formed thin film.

[0093]

The graph in Fig. 4 shows that the indentation hardness of the thin film tends to increase with increase in flow rate per unit time of the helium gas. The

graph in Fig. 5 shows that the Young's modulus of the thin film also tends to increase with increase in flow rate per unit time of the helium gas. According to the result in Fig. 4, for this film forming apparatus 1, if the flow rate per unit time of helium is changed to 45[sccm] or more in the above film forming condition of the phase shift film, the deposited film adhered to the inner wall surface of the shield 7 can have the indentation hardness of 5000[MPa] or more.

[0094]

Seemingly, it is enough to change the film forming condition of the phase shift film such that the flow rate per unit time of helium is 45[sccm] or more. However, if the flow rate per unit time of helium in the film forming condition of the phase shift film is increased, an amount of nitrogen incorporated into the phase shift film during forming the phase shift film by the reactive sputtering slightly decreases, while an amount of helium incorporated into the phase shift film increases. Even if the change in composition of the phase shift film is not so large, the optical property relatively greatly changes. Therefore, the film forming condition per se of the phase shift film cannot be changed.

[0095]

Based on the above results, the film forming apparatus 1 was started up according to Example of the present invention. Specifically, a mixed target 9 of molybdenum (Mo) and silicon (Si) (at% ratio of Mo:Si=4:96) bonded on the backing plate 8 via an indium bonding material was prepared first. The lower shield 71 and upper shield 72 were attached into the film forming chamber 2 of the DC magnetron sputtering type film forming apparatus 1, and the target 9 was then attached to the cathode 4. After evacuating the interior of the film forming chamber 2, a dummy substrate was placed on the substrate stage 3. Only the argon gas was then introduced from the gas inflow section 5 into the film forming chamber 2 at a flow rate of 15[sccm], and voltage was applied to the cathode 4 (target 9) at power of 0.4[kW], thereby generating plasma of the argon gas only within the film forming chamber 2. Argon particles were then caused to collide with the target 9 to relatively weakly clean the surface of the target 9 (the step of forming the lowermost layer film). Subsequently, the power to the cathode 4 was increased to 1.4[kW] to relatively vigorously clean the surface of the target 9 (the step of forming the lowermost layer film).

[0096]

The relatively weak cleaning and relatively vigorous cleaning removed contaminations such as organic matters attached to the surface of the target 9, or the oxide film on the surface layer. During the relatively weak cleaning and relatively vigorous cleaning, particles of molybdenum and silicon flew out of the surface of the target 9 to deposit, as the lowermost layer film, on the inner wall surface of the shield 7. While the lowermost layer film has the indentation hardness of less than 5000[MPa], its Young's modulus is less than 10000[MPa], and thus, it has high durability to the thermal expansion of the shield 7.

[0097]

Next, the supply of power to the cathode 4 was ceased, and a mixed gas of nitrogen ( $N_2$ ), argon (Ar), and helium (He) was introduced from the gas inflow section 5 into the film forming chamber 2 at a set flow rate (flow rate ratio [sccm] of  $N_2:Ar:He=18:9:50$ , pressure=0.3Pa). Once the flow rate ratio of the mixed gas in the film forming chamber 2 was stable, voltage was applied to the cathode 4 (target 9) at power of 2.4[kW] to cause the reactive sputtering, thereby forming the lower layer film made of the material containing molybdenum, silicon, and nitrogen (MoSiN film) on the lowermost layer film formed on the inner wall surface of the shield 7 (step of forming the lower layer film). According to the result in Fig. 4, this lower layer film has the indentation hardness of approximately 5500[MPa], i.e., 5000[MPa] or more.

[0098]

In this step of forming the lower layer film, every time the MoSiN film having a thickness of 60nm was formed on one dummy substrate, the dummy substrate was exchanged, and thus, thirty dummy substrates were used here. Therefore, the thickness of the lower layer film (MoSiN film) which was formed on the lowermost layer film formed on the inner wall surface of the shield 7 would be approximately  $1.8\mu m$  on average.

[0099]

Then, the supply of power to the cathode 4 was ceased, and the flow rate ratio of the mixed gas introduced from the gas inflow section 5 into the film forming chamber 2 was changed to the above flow rate ratio (flow rate ratio [sccm] of  $N_2:Ar:He=18:9:30$ ) and pressure (pressure=0.3Pa) for forming the phase shift film. Once the flow rate ratio of the mixed gas in the film forming chamber 2 was stable, voltage was applied to the cathode 4 (target 9) at power of 2.4[kW] to cause the reactive sputtering, thereby forming the upper layer film made of the material containing molybdenum, silicon, and nitrogen (MoSiN film) on the lower layer film formed on the inner wall surface of the shield 7 (step of forming the upper layer film). According to the result in Fig. 4, this upper layer film has the indentation hardness of approximately 3145[MPa], i.e., less than 5000[MPa]. As a result of this step, the surface state of the target 9 was substantially the same as the surface state in the reactive sputtering for forming the phase shift film.

[0100]

Also in this step of forming the upper layer film, every time the MoSiN film having a thickness of 60nm was formed on one dummy substrate, the dummy substrate was exchanged, and thus, thirty dummy substrates were used here. Therefore, the thickness of the upper layer film (MoSiN film) which was formed on the lower layer film formed on the inner wall surface of the shield 7 would be approximately  $1.8\mu m$  on average.

[0101]

The film forming apparatus 1 started up through the above procedure was

used to carry out the step of forming the phase shift film by the reactive sputtering on the substrate 100 made of synthetic quartz glass. Specifically, the substrate 100 was placed on the substrate stage, the mixed gas of nitrogen ( $N_2$ ), argon (Ar), and helium (He) was introduced from the gas inflow section 5 into the film forming chamber 2 at a set flow rate (flow rate ratio [sccm] of  $N_2:Ar:He=18:9:30$ , pressure=0.3Pa). Once the flow rate ratio of the mixed gas in the film forming chamber 2 was stable, voltage was applied to the cathode 4 (target 9) at power of 2.4[kW] to cause the reactive sputtering, thereby forming the phase shift film made of MoSiN and having a thickness of 61nm on the substrate 100.

[0102]

This step of forming the phase shift film was performed on one hundred substrates 100. Next, the one hundred substrates 100 on which the phase shift films were formed were subjected to defect inspection for the phase shift films using a mask blank defect inspection device (M6640: manufactured by Lasertec Corporation). Then, the selection step was carried out based on an acceptance criterion which accepted phase shift films with no defect of about 100nm size detected in the defect inspection. As a result, fifty one substrates among one hundred substrates were able to be selected as satisfying the acceptance criterion. A ratio (yield) of accepted products was significantly improved relative to the phase shift films formed on the substrates using the film forming apparatus started up by the conventional starting-up method.

[0103]

As a comparative example, the phase shift film was formed on the substrate using the film forming apparatus started up by the conventional starting-up method. The starting-up method in this comparative example was similar to the above Example in the step of forming the lowermost layer film on the inner wall surface of the shield 7. The difference from the starting-up method of Example 1 was that the same step as the step of forming the upper layer film was carried out without the step of forming the lower layer film on the lowermost layer film deposited on the inner wall surface of the shield 7. However, the step of forming the upper layer film in the comparative example was applied to sixty dummy substrates. Thus, in this comparative example, the thickness of the upper layer film (MoSiN film) which was formed on the lowermost layer film formed on the inner wall surface of the shield 7 would be approximately  $3.6\mu m$  on average.

[0104]

The film forming apparatus 1 started up by the starting-up method according to the comparative example was used to carry out the step of forming the phase shift film by the reactive sputtering on the substrate 100 made of synthetic quartz glass as in Example. Further, one hundred substrates 100 on which the phase shift films of the comparative example were formed were subjected to defect inspection for the phase shift films using the mask blank defect inspection device (M6640: manufactured by Lasertec Corporation). Then, the selection step was carried out based on the acceptance criterion which accepted phase shift films with

no defect of about 100nm size detected in the defect inspection. As a result, twenty nine substrates among one hundred substrates were selected as satisfying the acceptance criterion. A ratio (yield) of accepted products is regarded as significantly low.

[Manufacture of the mask blank]

[0105]

Then, the substrates 100 having the phase shift films selected as accepted products at the selection step in Example were placed respectively within the film forming chamber of another DC magnetron sputtering type film forming apparatus. A chromium (Cr) target was used, and a mixed gas of argon (Ar), carbon dioxide ( $\text{CO}_2$ ), nitrogen ( $\text{N}_2$ ), and helium (He) was used as a sputtering gas, so as to conduct the reactive sputtering, thereby forming the respective light-shielding films made of  $\text{CrOCN}$  ( $\text{Cr}:\text{O}:\text{C}:\text{N} = 55\text{at\%}:22\text{at\%}:12\text{at\%}:11\text{at\%}$ ) and having a thickness of 46nm on the respective phase shift films. The composition of the above described light-shielding films was analyzed by X-ray Photoelectron Spectroscopy (XPS: with Rutherford Backscattering Spectrometry (RBS) correction). The optical density (OD) of the laminated structures comprised of the respective phase shift films and light-shielding films at a wavelength of 193nm as measured was 3.0 or more.

[0106]

Then, the substrates 100 on which the respective phase shift films and light-shielding films were laminated were placed respectively into an RF magnetron sputtering type film forming apparatus, a silicon dioxide ( $\text{SiO}_2$ ) target was used, and an argon (Ar) gas was used as a sputtering gas, so as to perform RF sputtering, thereby forming the respective hard mask films made of silicon and oxygen and having a thickness of 5nm on the respective light-shielding films. With the above method, the mask blanks of Example, each having a structure in which the phase shift film, light-shielding film, and hard mask film were laminated on the substrate 100, were manufactured.

[0107]

[Manufacture of the phase shift mask]

Then, the mask blanks manufactured using the film forming apparatus started up by the method for starting up a film forming apparatus according to Example were used to fabricate respective phase shift masks according to Example through the following procedure. First, the HMDS treatment was applied to respective surfaces of the hard mask films. Subsequently, resist films, each made of a chemically amplified resist for electron beam lithography and having a film thickness of 100nm, were formed on the respective surfaces of the hard mask films by a spin coating method. Then, the resist films were subjected to electron beam lithography of respective first patterns that were phase shift patterns to be formed in the phase shift films, and a predetermined development treatment was conducted, thereby forming first resist patterns having the respective first patterns.

[0108]

Next, the dry etching with a  $\text{CF}_4$  gas using the first resist patterns as masks was performed, and the first patterns were formed in the respective hard mask films. Then, the first resist patterns were removed by ashing, or by a peeling liquid or the like. Subsequently, the dry etching with a mixed gas of chlorine and oxygen (gas flow rate ratio of  $\text{Cl}_2:\text{O}_2=4:1$ ) using the hard mask films having the respective first patterns as masks was performed, so that the first patterns (first light-shielding patterns) were formed in the light-shielding films. Then, the dry etching with a fluorine-based gas ( $\text{SF}_6+\text{He}$ ) using the light-shielding films having the respective first patterns as masks was performed, such that the first patterns (phase shift patterns) were formed in the phase shift films while at the same time the hard mask films were removed.

[0109]

Then, resist films, each made of a chemically amplified resist for electron beam lithography and having a film thickness of 150nm, were formed on the respective light-shielding films by the spin coating method. Next, the resist films were subjected to exposure lithography of respective second patterns that were patterns to be formed in the light-shielding films (light-shielding patterns), and a predetermined treatment such as a development treatment was conducted, thereby forming second resist patterns having the respective light-shielding patterns. Subsequently, the dry etching with a mixed gas of chlorine and oxygen (gas flow rate ratio of  $\text{Cl}_2:\text{O}_2=4:1$ ) using the second resist patterns as masks was performed, such that second patterns (light-shielding patterns) were formed in the light-shielding films. Further, the second resist patterns were removed, and the predetermined treatment such as cleaning was conducted, so as to obtain the phase shift masks according to Example.

[0110]

The halftone phase shift masks manufactured according to Example were subjected to mask pattern inspection using a mask inspection device, and as a result, no defect due to the phase shift films was detected. The phase shift masks manufactured with high accuracy were confirmed.

[0111]

Using AIMS193 (manufactured by Carl Zeiss), a simulation of a transfer image in the exposure transfer to a resist film on a semiconductor device with the exposure light at the wavelength of 193nm was performed on each halftone phase shift mask of Example. As a result of inspection of the transfer images exposed in this simulation, they satisfied the design specification sufficiently. According to this result, even if the phase shift mask of Example is set on the mask stage of the exposure apparatus to perform the exposure transfer to the resist film on the semiconductor device, the circuit pattern finally formed on the semiconductor device may be thought of as having great accuracy.

Reference Numerals

[0112]

- 1: film forming apparatus
- 2: film forming chamber
- 3: substrate stage
- 31: rotary shaft
- 4: cathode
- 5: gas inflow section
- 6: gas discharging section
- 7: shield
- 71: lower shield
- 72: upper shield
- 8: backing plate
- 9: target
- 21: central axis
- 22: straight line

What is claimed is:

1. A method for starting up a film forming apparatus including a target made of a material containing a transition metal and silicon and a shield in a film forming chamber, characterized in that the method comprises the steps of:

introducing a noble gas and a reactive gas into the film forming chamber and forming a lower layer film on a surface of the shield by reactive sputtering, wherein the lower layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of 5000MPa or more in accordance with a nanoindentation method; and

introducing a noble gas and a reactive gas into the film forming chamber and forming an upper layer film on the lower layer film on the shield by reactive sputtering, wherein the upper layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

2. The method for starting up a film forming apparatus according to claim 1, characterized in that the noble gas is a mixed gas of helium and one or more gases selected from argon, krypton, and xenon.

3. The method for starting up a film forming apparatus according to claim 2, characterized in that a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the lower layer film is greater than a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the upper layer film.

4. The method for starting up a film forming apparatus according to any one of claims 1 to 3, characterized in that the reactive gas in the step of forming the lower layer film and the step of forming the upper layer film at least includes a gas containing nitrogen.

5. The method for starting up a film forming apparatus according to any one of claims 1 to 4, characterized in that a ratio of the content of the transition metal divided by the total content of the transition metal and silicon in the target is less than 34%.

6. A method for manufacturing a mask blank using the film forming apparatus started up by the method for starting up a film forming apparatus according to any one of claims 1 to 5, characterized in that:

the mask blank includes at least a thin film for pattern formation on a substrate; and

the method comprises the step of:

placing the substrate on a substrate stage provided in the started-up film

forming apparatus, introducing a noble gas and a reactive gas into the film forming chamber, and forming the thin film for pattern formation on a main surface of the substrate by reactive sputtering, wherein the thin film for pattern formation is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

7. A method for manufacturing a mask blank using a film forming apparatus including a target made of a material containing a transition metal and silicon, a shield, and a substrate stage in a film forming chamber, characterized in that:

the mask blank includes at least a thin film for pattern formation on a substrate; and

the method comprises the steps of:

introducing a noble gas and a reactive gas into the film forming chamber and forming a lower layer film on a surface of the shield by reactive sputtering, wherein the lower layer film is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of 5000MPa or more in accordance with a nanoindentation method; and

placing the substrate on the substrate stage in the film forming chamber, introducing a noble gas and a reactive gas into the film forming chamber, and forming the thin film for pattern formation on a main surface of the substrate by reactive sputtering, wherein the thin film for pattern formation is made of a material containing the transition metal, silicon, and elements derived from the reactive gas, and has indentation hardness of less than 5000MPa in accordance with the nanoindentation method.

8. The method for manufacturing a mask blank according to claim 7, characterized in that during the step of forming the thin film for pattern formation, a deposited film made of the same material as the material constituting the thin film for pattern formation is also formed on the lower layer film on the shield.

9. The method for manufacturing a mask blank according to claim 7 or 8, characterized in that the noble gas is a mixed gas of helium and one or more gases selected from argon, krypton, and xenon.

10. The method for manufacturing a mask blank according to claim 9, characterized in that a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the lower layer film is greater than a ratio of a flow rate per unit time of a helium gas in the noble gas introduced into the film forming chamber divided by a total flow rate per unit time of the noble gas in the step of forming the thin film for pattern formation.

11. The method for manufacturing a mask blank according to any one of claims 7 to 10, characterized in that the reactive gas in the step of forming the lower layer film and the step of forming the thin film for pattern formation at least includes a

gas containing nitrogen.

12. The method for manufacturing a mask blank according to any one of claims 7 to 11, characterized in that a ratio of the content of the transition metal divided by the total content of the transition metal and silicon in the target is less than 34%.

13. A method for manufacturing a transfer mask, characterized in that the method comprises the step of using the mask blank manufactured by the method for manufacturing a mask blank according to any one of claims 6 to 12 to form a transfer pattern in the thin film for pattern formation by dry etching.

14. A method for manufacturing a semiconductor device, characterized in that the method comprises the step of using the transfer mask manufactured by the method for manufacturing a transfer mask according to claim 13 to transfer the transfer pattern to a resist film on a semiconductor substrate by exposure.