

METHOD OF MANUFACTURING MASK BLANK, METHOD OF MANUFACTURING TRANSFER MASK, AND METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE

5 TECHNICAL FIELD

The present disclosure relates to a method of manufacturing a mask blank, a method of manufacturing a transfer mask and a method of manufacturing a semiconductor device.

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BACKGROUND

Generally, in a manufacturing process of a semiconductor device, photolithography is used to form a fine pattern. In the formation of the fine pattern, multiple transfer masks
15 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:
20 193nm), that is, shorter wavelength light sources are increasingly used.

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.
25 The sputtering apparatus for carrying out the sputtering process generally includes a sputtering target and a substrate holder positioned within a vacuum chamber. The sputtering target may be surrounded by a shield.

During the sputtering process sputtering particles may adhere to the shield and form
30 a film on the shield. If this thin film peels off the shield it may form particles which can land on the substrate and generate defects. This reduces yields from the manufacturing process of mask blanks.

SUMMARY

According to a first aspect of the present disclosure, a method of manufacturing a mask blank comprising a thin film for pattern formation on a substrate is provided. The method comprises: a step of arranging a target containing one or more elements
5 selected from silicon and metal in a vacuum chamber and forming a thin film by sputtering the target to an atmosphere including noble gas, wherein a shield is set around the target in the vacuum chamber, the shield being coupled to one or more support members, and wherein an amount of heat transferred Q from the shield through all of the support members is 100 W or more.

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By configuring the support members such that the amount of heat transferred from the shield through all of the support members is 100 W or more, it is possible to limit temperature fluctuations of the shield. This allows the suppression of the generation of particles caused by peel off from the shield due to expansion and contraction caused
15 by the temperature fluctuations.

In some embodiments, the amount of heat transferred Q from the shield through all of the support members is 200 W or more, preferably 500 W or more and more preferably 800 W or more.

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The material of the support members may be selected to have a thermal conductivity of 50 W/(mm°C) or greater or preferably a thermal conductivity of 100 W/(mm°C) or greater.

25 The one or more support members may be formed from a material comprising one of more of the following: aluminium, cast iron, copper and brass. Preferably, the material of the one or more support members comprises aluminium.

In some embodiments, the target contains metal and silicon.

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In some embodiments, the atmosphere includes noble gas and reactive gas.

According to a second aspect of the present disclosure, a method for manufacturing a transfer mask is provided, the method comprises a step of forming a transfer pattern

on the thin film of a mask blank manufactured by the method for manufacturing a mask blank set out above by dry etching.

According to a third aspect of the present disclosure, a method manufacturing a semiconductor device is provided. The method comprises a step of exposure-transferring a transfer pattern on a resist film on a semiconductor substrate using a transfer mask manufactured by the method for manufacturing a transfer mask set out above.

10 BRIEF DESCRIPTION OF THE DRAWINGS

In the following, embodiments of the present invention will be described as non-limiting examples with reference to the accompanying drawings in which:

15 FIG.1 is a schematic view showing an example of a film forming apparatus used in methods according to embodiments of the present invention;

FIG.2A to FIG.2C show views of a prior art cathode shield and cathode shield support members;

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FIG.3A to FIG.3C show views of a cathode shield and cathode shield support members according to an embodiment of the present invention;

FIG.4A to FIG.4C show views of a cathode shield and cathode shield support members according an embodiment of the present invention;

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FIG.5 is a graph showing a comparison of cathode shield temperature against time for different cathode shield support members;

30 FIG.6 is a cross-sectional view showing a structure of a mask blank of an embodiment of this invention; and

FIG.7 is a schematic cross-sectional view showing a manufacturing step of the phase shift mask of an embodiment of this invention.

DETAILED DESCRIPTION

5 In a conventional apparatus forming a thin film on a mask blank, a cathode shield is placed around the target to protect the cathode components from deposition during sputtering. For example, a DC sputtering cathode has standardized metal shaft support members to support the cathode shield and to accommodate most designs of cathode shield. To maintain constant cathode shield temperature, a heater lamp assembly is provided around the cathode. Cooling water is circulated throughout the
10 target cooling plate so that additional heat from the cathode shield can be dissipated.

In the above design, the metal shaft support members support the cathode shield and transfer additional heat from the cathode shield through conductive heat transfer to maintain constant temperature. However, the conductive heat transfer is limited by
15 the small contact area of the metal shaft support members. As sputtering power can sometimes be very high reaching thousands of Watts, the temperature will rise above the set temperature. As a result, the cathode shield will experience large temperature fluctuation due to insufficient cooling. The cathode shield will undergo thermal expansion and contraction, generating film thermal stress on cathode shield due to
20 mismatch thermal expansion coefficient between the aluminium cathode shield and a film formed by sputtering particles on the cathode shield. Once the thermal stress exceeds the film adhesion, the film will peel off from the cathode shield and fall on the substrates being processed.

25 FIG.1 is a schematic view showing an example of a film forming apparatus used in methods according to embodiments of the present invention. The film forming apparatus 10 is for forming a thin film for pattern formation on a main surface of a substrate 100 by reactive sputtering. The film forming apparatus 10 comprises a film forming chamber 20, a substrate stage 30, a cathode 40, a gas inflow section 50, a
30 gas discharging section 60, a shield 70 which is formed from a lower shield 71 and an upper shield 72. The cathode 40 is surrounded by a cathode shield 80. The substrate stage 30 on which the substrate 100 is to be placed is provided with a rotary shaft 31 extending through a lower wall of the film forming chamber 20. A target 90 is attached

to the cathode 40 with a backing plate 41 therebetween. The shield 70 is provided such that sputtering particles flying out of the target 90 are prevented from adhering to the inner wall surface of the film forming chamber 20 during sputtering by the film forming apparatus 10. The cathode shield 80 is formed from a metal such as aluminium. The cathode shield 80 is supported by cathode shield support members 81 which are coupled to a water cooled heat sink 82 located on the film forming chamber 20. In addition to supporting the cathode shield 80, the cathode shield support members 81 also act to transfer heat away from the cathode shield 80.

In operation to manufacture a mask blank, a film forming gas, i.e., a mixed gas of a noble gas and a reactive gas, is introduced from the gas inflow section 50 into the film forming chamber 20. Then, the film forming gas in the film forming chamber 20 is discharged from the gas discharging section 60. The gas discharging section 60 is also used to evacuate the film forming chamber 20 to a predetermined degree of vacuum. A plurality of gas inflow sections 50 may be provided in the film forming chamber 20. For example, the inflow section for noble gas inflow and the inflow section for reactive gas inflow, i.e., two gas inflow sections 50, may be provided in the film forming chamber 20, or alternatively, inflow sections for respective types of gases may be provided in the film forming chamber 20.

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 20 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 73. 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 20 (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 70 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 70 is further preferably made of aluminium, iron, copper, etc.

During the sputtering process, sputtering particles ejected from the target 90 may land on the cathode shield 80 and form a film on the cathode shield.

In the configuration shown in FIG.1, the cathode shield support members 81 support and transfer additional heat from the cathode shield 80 through conductive heat transfer to maintain constant temperature. However, the conductive heat transfer is limited by the contact area of the cathode shield support members 81. As sputtering power can sometimes be very high reaching a few thousand Watts, the temperature will rise above the set temperature.

As a result, the cathode shield 80 will experience large temperature fluctuation due to insufficient cooling. The cathode shield 80 will undergo thermal expansion and contraction, generating film thermal stress on cathode shield 80 due to mismatch thermal expansion coefficient between the cathode shield 80 and the film formed on the cathode shield 80. Once the thermal stress exceeds the film adhesion, the film will peel off from the cathode shield and fall on to the substrate 100 being processed.

This peel off process leads to defects in the mask blanks being formed and reduces production yields.

FIG.2A is a side view of a cathode shield and cathode shield support members of a conventional film forming apparatus. FIG.2B is a view of a cathode shield support member of a conventional film forming apparatus. FIG.2C is a perspective view of a cathode shield and cathode shield support members of a conventional film forming apparatus.

The cathode shield 80A has a front face 800A that forms an annulus. There is a spherical cavity 801A in the centre which receives the cathode. Six cathode shield support members 81A are arranged around the circumference of the cathode shield 80A and extend from the rear of the annular face 800A parallel to the spherical cavity 801A.

The cathode shield support members 81A are elongate cylinders. A threaded hole 811A is provided in the upper end to allow the cathode shield support members 81A

to be bolted to the cathode shield 80A. A threaded bolt 813A extends from the lower end of the cathode shield support members 81A to allow the cathode shield support members 81A to be attached to a heatsink.

- 5 The conventional cathode shield support members 81A shown in FIG.2A to 2C are formed from grade 304 stainless steel.

FIG.3A is a side view of a cathode shield and cathode shield support members of a film forming apparatus according to an embodiment of the present invention. FIG.3B
10 is a view of a cathode shield support member according an embodiment of the present invention. FIG.3C is a perspective view of a cathode shield and cathode shield support members according to an embodiment of the present invention.

The cathode shield 80A shown in FIG.3A and FIG.3C corresponds to that shown in
15 FIG.2A and FIG.2C. The configuration of the cathode shield support members 81B shown in FIG.3A to 3C corresponds to those shown in FIG.2A to FIG.2C, however, the cathode shield support member 81B shown in FIG.3A to FIG.3C is formed from an aluminium based alloy (for example, aluminium 6061.).

20 As shown in FIG.3B, the cathode shield support members 81B are elongate cylinders. A threaded hole 811B is provided in the upper end to allow the cathode shield support members 81B to be bolted to the cathode shield 80A. A threaded bolt 813B extends from the lower end of the cathode shield support members 81B to allow the cathode shield support members 81B to be attached to a heatsink.

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FIG.4A is a side view of a cathode shield and cathode shield support members of a film forming apparatus according to an embodiment of the present invention. FIG.4B
is a view of a cathode shield support member according an embodiment of the present invention. FIG.4C is a perspective view of a cathode shield and cathode shield support
30 members according to an embodiment of the present invention.

The cathode shield 80A shown in FIG.4A and FIG.4C corresponds to that shown in FIG.2A and FIG.2C. The configuration of the cathode shield support members 81C differs from that shown in FIG.2B and FIG.3B. As shown in FIG.4B, the cathode shield

support members 81C of this embodiment have an upper surface 815C which is substantially rectangular. The cathode shield support members 81C have a square hole 812C in running through the centre and a lower surface 816C which has a shape corresponding to the shape of the upper surface 815C. A first bolt hole 811C runs from the upper surface 815C to the top of the hole 812C and a second bolt hole 813C runs from the bottom of the hole 812C to the lower surface 816C.

As shown in FIG.4A and FIG.4C, six cathode shield support members 81C are arranged around the circumference of the cathode shield 80A and extend from the rear of the annular face 800A parallel to the spherical cavity 801A. The cathode shield support members 81C are attached to the cathode shield 80A by bolts running through the first bolt holes 811C and are attached to the heatsink by bolts running through the second bolt holes 813C. It is noted that the positions of the first bolt holes 811C and the second bolt hole 813C correspond to the positions of the threaded hole 811A the threaded bolt 813A of the conventional cathode shield support member 81A shown in FIG.2B, therefore, the cathode shield support members 81C shown in FIG.4B can be used with an existing cathode shield without the need to make additional alterations because the positioning of the bolt holes corresponds to the position of fixing holes in the cathode shield and heatsink of a conventional film forming apparatus.

The cathode shield support members 81C shown in FIG.4A to FIG.4C are formed from aluminium.

As the contact area of the upper surface 815C and the lower surface 816C of the cathode shield support members 81C shown in FIG.4B greater than that of the cathode shield support members 81A shown in FIG.2B, the heat transfer from the cathode shield to the heatsink is increased and therefore temperature fluctuations in the cathode shield can be reduced. In addition to adjusting the design of the cathode shield supports, it is also possible to increase the heat transfer by changing the material of the cathode shield support members. For example, the cathode shield support members 81B shown in FIG.3B are formed from an aluminium based alloy which has a higher thermal conductivity than stainless steel which is used to form the cathode shield support members 81A shown in FIG.2B.

In order to demonstrate the effects of the modifications to the cathode shield support members described above, simulations of the temperature fluctuations were carried out.

- 5 As film forming sputtering processes typically employs high power, the cathode shield surrounding the target undergoes large temperature fluctuation from a minimum temperature of 120°C to a maximum temperature of 145°C due to the hot impinging target molecules. The cathode shield support members are connected to the cathode heat sink at 9°C to dissipate the additional heat.

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In order to simulate the conductive heat transfer, Fourier's Law is studied.

$$Q = -kA \frac{dT}{dx}$$

Here, Q is the amount of heat transfer (W), k is the thermal conductivity (W/(mm°C)), A is the contact area (mm²) and $\frac{dT}{dx}$ is the temperature gradient (°C/mm).

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Simulations were carried out using Siemens NX FEA software. To determine the heat flux through different materials, a cathode shield at 120°C and a cathode heat sink with circulating water of forced convective heat transfer coefficient 0.003W/mm²°C is simulated. The heat loads from the sputtering process to the cathode shield are estimated to be 300W from the hot impinging target molecules as it is able to propel the cathode shield temperature to 130°C within 500s process time.

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A comparative example corresponding to the cathode shield support members shown in FIG.2B and five examples were simulated.

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The first example corresponds to the embodiment shown in FIG.3B. Examples 2 to 5 correspond to configurations similar to that shown in FIG.4B with differing contact areas.

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For the comparative example and example 1, the contact area for each cathode shield support member was calculated as 134.3mm² as annulus not including the area of the bolt hole. For examples 1 to 5, the contact areas were calculated as the area of the vertical portions 817C and not including the area overlapping the hole 812C.

Thus, the contact areas for the comparative example and examples 1 to 5 are as follows.

Material	Stainless Steel 304	Aluminium 6061				
	Comparative example	Example 1	Example 2	Example 3	Example 4	Example 5
Contact Area (mm ²)	134.3	134.3	178.1	365.68	714.1	1027.84

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FIG.5 shows the results of the simulation. In each case, a cathode shield was simulated being coupled to six cathode shield support members. As can be seen from FIG.5, for the comparative example, the cathode shield increased in temperature from 120°C to 130°C over the simulation period of 500 seconds. By changing the material from stainless steel to aluminium, this temperature fluctuation could be reduced. Further, by increasing the contact surface area the temperature fluctuation could be greatly reduced. It is noted that example 3 exhibited a small temperature fluctuation of less than 1°C and examples 4 and 5 exhibited negligible temperature fluctuation.

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The total heat transfer through the six cathode shield support members can be calculated as follows:

Comparative example:

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$$\begin{aligned}
 Q &= \text{Thermal flux towards heat sink direction} \times \text{Contact Area} \times 6 \\
 &= 0.023 \times 134.3 \times 6 \\
 &= 18.53W
 \end{aligned}$$

25 Example 1:

$$\begin{aligned}
 Q &= \text{Thermal flux towards heat sink direction} \times \text{Contact Area} \times 6 \\
 &= 0.151 \times 134.3 \times 6
 \end{aligned}$$

$$= 121.68W$$

Example 2:

$$\begin{aligned} 5 \quad Q &= \text{Thermal flux towards heat sink direction} \times \text{Contact Area} \times 6 \\ &= 0.135 \times 178.1 \times 6 \\ &= 144.26W \end{aligned}$$

10 Example 3:

$$\begin{aligned} Q &= \text{Thermal flux towards heat sink direction} \times \text{Contact Area} \times 6 \\ &= 0.135 \times 365.68 \times 6 \\ &= 296.2W \end{aligned}$$

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Example 4:

$$\begin{aligned} Q &= \text{Thermal flux towards heat sink direction} \times \text{Contact Area} \times 6 \\ &= 0.135 \times 714.1 \times 6 \\ 20 \quad &= 578.42W \end{aligned}$$

Example 5:

$$\begin{aligned} Q &= \text{Thermal flux towards heat sink direction} \times \text{Contact Area} \times 6 \\ 25 \quad &= 0.135 \times 1027.84 \times 6 \\ &= 832.55W \end{aligned}$$

As can be seen from FIG.5, if the total heat transfer is increased to above 100W, there is an impact on the temperature fluctuation of the cathode shield. Further by increasing the heat transfer to above 200W, 500W or 800W, the temperature fluctuation can be greatly reduced.

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In the examples discussed above, the total heat transfer is increased by modifications to the shape of the cathode support members and by changing the material of the cathode shield support members from stainless steel to aluminium. Other materials may be used as shown in the table below. In particular, if a material having a thermal conductivity of 50 W/mm.°C or greater or 100 W/mm.°Cm a significant increase in the heat transfer compared to stainless steel will result and therefore the temperature fluctuation of the cathode shield can be reduced.

Material	Heat Flux (W/mm ²)	Thermal Conductivity (W/mm.°C)
Stainless Steel 304	0.023	16.3
Aluminium 6061	0.151	154.25
Cast Iron	0.064	52
Copper	0.216	387
Brass	0.116	116

It is noted that copper has the highest thermal conductivity of the material listed in the table, however, the cost of copper is significantly higher than that of aluminium and therefore aluminium represents a balance between thermal performance and cost.

FIG.6 is a cross-sectional view showing a structure of a mask blank 100 for forming a phase shift mask according to an embodiment of this invention. The mask blank 100 shown in FIG.6 is for manufacturing a phase shift mask, having a structure where a phase shift film (thin film for pattern formation) 2, a light shielding film 3, and a hard mask film 4 are stacked in this order on a transparent substrate 1.

The phase shift film 2 is required to have a transmittance to an exposure light of 1% or more. At least 1% transmittance to an exposure light is necessary to generate sufficient phase shifting effect between the exposure light transmitted through the interior of the phase shift film and the exposure light transmitted through the air. The transmittance of the phase shift film to an exposure light is preferably 2% or more, and more preferably 3% or more. On the other hand, the transmittance of the phase shift

film to an exposure light is preferably 40% or less, more preferably 20% or less, and even more preferably 10% or less.

5 To obtain a proper phase shifting effect, it is necessary for the phase shift film 2 to be adjusted so as to generate a phase difference in the range of 150 degrees or more and 240 degrees or less between the transmitting exposure light and the light transmitted through the air for the same distance as the thickness of the phase shift film 2. The lower limit of the phase difference in the phase shift film 2 is preferably 155 degrees or more, and more preferably 160 degrees or more. On the other hand,
10 the upper limit of the phase difference in the phase shift film 2 is preferably 210 degrees or less, and more preferably 190 degrees or less.

From the viewpoint of reducing EMF (Electro-Magnetic Field) bias of the phase shift mask manufactured from the mask blank 100, the phase shift film 2 is required to have
15 a thickness of less than 100nm, more preferably 90nm or less, and even more preferably 80nm or less. On the other hand, it is necessary for the thickness of the phase shift film 2 to obtain a proper phase shifting effect as mentioned above, which is required to be 50nm or more, and preferably 55nm or more.

20 The phase shift film 2 is often formed in contact with a surface of the transparent substrate 1. Incidentally, the phase shift film 2 does not have to be formed in contact with a surface of the transparent substrate 1, and an etching stopper film can be provided between the transparent substrate 1 and the phase shift film 2. In this case, the thickness of the etching stopper film should be 10nm or less, preferably 7nm or
25 less, and more preferably 5nm or less. Further, on the viewpoint of effectively functioning as an etching stopper, the thickness of the etching stopper film should be 3nm or more. The etching stopper film is preferably made of a material containing chromium, or a material containing silicon and aluminium.

30 In the case of applying an etching stopper film of a material containing silicon and aluminium, extinction coefficient k of the etching stopper film is preferably less than 0.1, more preferably 0.05 or less, and even more preferably 0.01 or less. Further, refractive index n of the etching stopper film in this case is preferably 1.9 or less, and

more preferably 1.7 or less. Refractive index n of the etching stopper film is preferably 1.55 or more.

5 The mask blank 100 has a light shielding film 3 on the phase shift film 2. Optical density in an outer peripheral region of a transfer mask including a phase shift mask is required to be at least 2.0 or more, preferably 2.5 or more, and more preferably 2.8 or more. The phase shift film 2 has a function to transmit an exposure light at a predetermined transmittance, and it is difficult to secure an optical density of a predetermined value with the phase shift film 2 alone. Therefore, it is necessary to
10 stack the light shielding film 3 on the phase shift film 2 at the stage of manufacturing the mask blank 100 to secure lacking optical density. With such a structure of the mask blank 100, the phase shift mask 200 securing a predetermined value of optical density on the outer peripheral region can be manufactured by removing the light shielding film 3 of the region using the phase shift effect (basically transfer pattern
15 forming region) during manufacture of the phase shift mask 200.

A single layer structure and a stacked structure of two or more layers are applicable to the light shielding film 3. Further, each layer in the light shielding film of a single layer structure and the light shielding film with a stacked structure of two or more layers
20 can be configured by approximately the same composition in the thickness direction of the layer or the film, or with a composition gradient in the thickness direction of the layer.

The mask blank 100 in FIG.6 is configured as a structure where the light shielding film
25 3 is stacked on the phase shift film 2 without an intervening film. For the light shielding film 3 in the case of this structure, it is necessary to apply a material having sufficient etching selectivity to etching gas used in forming a pattern on the phase shift film 2. The light shielding film 3 in this case is preferably formed from a material containing chromium. Materials containing chromium for forming the light shielding film 3 can
30 include, in addition to chromium metal, a material containing chromium and one or more elements selected from oxygen, nitrogen, carbon, boron, and fluorine.

While a chromium-based material is generally etched by mixed gas of chlorine-based gas and oxygen gas, etching rate of the chromium metal to the etching gas is not as

high. Considering enhancing etching rate of the mixed gas of chlorine-based gas and oxygen gas to etching gas, the material forming the light shielding film 3 preferably includes chromium and one or more elements selected from oxygen, nitrogen, carbon, boron, and fluorine. Further, one or more elements among molybdenum, indium, and tin can be included in the material containing chromium for forming the light shielding film 3. Including one or more elements among molybdenum, indium, and tin can increase etching rate to mixed gas of chlorine-based gas and oxygen gas.

On the other hand, this invention includes, as a mask blank 100 of another embodiment, a structure including another film (etching stopper film) between the phase shift film 2 and the light shielding film 3. In this case, it is preferable to form the etching stopper film from the material containing chromium mentioned above, and the light shielding film 3 from a material containing silicon or a material containing tantalum.

A material containing silicon for forming the light shielding film 3 can include a transition metal, and metal elements other than the transition metal can also be included. The reason is that when a transition metal is included in the light shielding film 3, light shielding performance is significantly improved compared to the case without the transition metal, and the thickness of the light shielding film 3 can be reduced. The transition metals to be included in the light shielding film 3 include any one of a metal such as molybdenum(Mo), 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), or a metal alloy thereof. Metal elements other than transition metal elements to be included in the light shielding film 3 include aluminium(Al), indium(In), tin(Sn), gallium(Ga), etc.

In the mask blank 100, a preferable structure is that a hard mask film 4 made of a material having etching selectivity to etching gas used in etching the light shielding film 3 is further stacked on the light shielding film 3. Since the light shielding film 3 must have a function to secure a predetermined optical density, there is a limitation to reduce its thickness. The film thickness of the hard mask film 4 is sufficient if the film thickness functions as an etching mask until the completion of dry etching for forming a pattern on the light shielding film 3 immediately below the hard mask film 4, and basically is not limited with regard to optical density. Therefore, the thickness of the

hard mask film 4 can be reduced significantly compared to the thickness of the light shielding film 3.

In the case where the light shielding film 3 is made of a material containing chromium, the hard mask film 4 is preferably made of the material containing silicon given above. Since the hard mask film 4 in this case tends to have low adhesiveness with the resist film of an organic material, it is preferable to treat the surface of the hard mask film 4 with HMDS (Hexamethyldisilazane) to enhance surface adhesiveness. The hard mask film 4 in this case is more preferably made of SiO₂, SiN, SiON, etc.

Further, in the case where the light shielding film 3 is made of a material containing chromium, materials containing tantalum are also applicable as the materials of the hard mask film 4, in addition to the material containing silicon given above. The material containing tantalum in this case includes, in addition to tantalum metal, a material containing tantalum and one or more elements selected from nitrogen, oxygen, boron, and carbon, for example, Ta, TaN, TaO, TaON, TaBN, TaBO, TaBON, TaCN, TaCO, TaCON, TaBCN, and TaBOCN. Further, in the case where the light shielding film 3 is made of a material containing silicon, the hard mask film 4 is preferably made of the material containing chromium given above.

In the mask blank 100, a resist film of an organic material is preferably formed in contact with the surface of the hard mask film 4 at a film thickness of 100nm or less. In the case of a fine pattern to meet DRAM hp32nm generation, a SRAF (Sub-Resolution Assist Feature) with 40nm line width may be provided on a transfer pattern (phase shift pattern) to be formed on the hard mask film 4. However, even in this case, cross-sectional aspect ratio of the resist pattern can be reduced down to 1:2.5 so that collapse and falling off of the resist pattern can be prevented in rinsing and developing, etc. of the resist film. The resist film preferably has a film thickness of 80nm or less.

The step of forming a thin film includes placing a transparent substrate on a substrate stage in a film-forming apparatus, introducing at least nitrogen-based gas and noble gas in the film-forming apparatus, applying voltage on a target containing a metal and silicon, and through reactive sputtering, forming a thin film for pattern formation on a main surface of the transparent substrate. The procedure of the reactive sputtering is

as mentioned above. Nitrogen gas or nitrogen compound gas is applied as the nitrogen-based gas to be introduced into the film-forming apparatus. The nitrogen-based gas herein includes, e.g., N_2 , NO, NO_2 , NH_3 , and HNO_3 . Particularly, nitrogen-based gas herein is preferably nitrogen gas.

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Noble gas to be introduced into the film-forming apparatus can include helium, neon, argon, krypton, and xenon. Particularly, the noble gas herein is preferably mixed gas including helium and one or more gases selected from argon, krypton, and xenon. On the gas to be introduced into the film forming chamber, gas that is difficult to completely avoid mixture such as water vapor, gas in the atmosphere, outgas from members in the film forming chamber, etc. may be included within the scope of not affecting various properties required for a thin film formed through reactive sputtering.

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A target of the film-forming apparatus is made of a material containing a metal and silicon. The metal in the target is similar to the metal in the thin film for pattern formation. $M/[M+Si]$ ratio of the target is similar to $M/[M+Si]$ ratio in the thin film for pattern formation. In the case of applying DC sputtering for reactive sputtering of the thin film, the target requires a predetermined degree or more conductivity. Considering this point, $M/[M+Si]$ ratio of the target is preferably 2% or more.

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In the case where the thin film for pattern formation is a phase shift film, the method for manufacturing the mask blank according to this invention preferably includes a step of forming a light shielding film on the thin film (phase shift film) after the second heat treatment. This is because, in the case of manufacturing a phase shift mask using a mask blank manufactured through the method for manufacturing a mask blank according to this invention, a light shielding film is necessary to form a light shielding band, etc. as mentioned above. Further, in this case, the light shielding film is preferably made of a material containing chromium.

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The step of forming a light shielding film mentioned above includes placing a transparent substrate having a phase shift film on a substrate stage in a film-forming apparatus, at least introducing reactive gas and noble gas in the film-forming apparatus, applying voltage to a target containing chromium, and forming a light shielding film on the phase shift film through reactive sputtering. The method of the

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reactive sputtering is similar as above. The reactive gas to be introduced into the film-forming apparatus can include, e.g., N₂, O₂, NO, NO₂, and CH₄. Noble gas is similar to the case described above.

- 5 On the other hand, the method for manufacturing a transfer mask of the embodiment of this invention includes a step of forming a transfer pattern on the mask blank of the above embodiment, or the thin film for pattern formation of the mask blank manufactured by the method for manufacturing a mask blank of the above embodiment by dry etching. Fluorine-based gas is used for etching gas in dry etching
10 of the thin film for pattern formation.

The above method for manufacturing a transfer mask is suitable for the manufacture of a phase shift mask. The method for manufacturing the phase shift mask 200 of this invention according to the embodiment is explained below according to the
15 manufacturing steps shown in FIG.8. The method explained herein is the method for manufacturing the phase shift mask 200 using the mask blank 100 having the hard mask film 4 stacked on the light shielding film 3. Further, a material containing chromium is applied to the light shielding film 3, and a material containing silicon is applied to the hard mask film 4.

20 First, a resist film was formed in contact with the hard mask film 4 of the mask blank 100 by spin coating. Next, a first pattern, which is a transfer pattern (phase shift pattern) to be formed on the phase shift film, was exposed and drawn with an electron beam on the resist film, and predetermined treatments such as developing were
25 further conducted, to thereby form a first resist pattern 5a having a phase shift pattern (see FIG.7(a)). Subsequently, dry etching was conducted using fluorine-based gas with the first resist pattern 5a as a mask, and a first pattern (hard mask pattern 4a) was formed on the hard mask film 4 (see FIG.7(b)).

30 Next, after removing the first resist pattern 5a, dry etching was conducted using mixed gas of chlorine-based gas and oxygen gas with the hard mask pattern 4a as a mask, and a first pattern (light shielding pattern 3a) was formed on the light shielding film 3 (see FIG.7(c)). Subsequently, dry etching was conducted using fluorine-based gas with the light shielding pattern 3a as a mask, and a first pattern (phase shift pattern

2a) was formed on the phase shift film 2, and at the same time the hard mask pattern 4a was removed (see FIG.7(d)).

Next, a resist film was formed on the mask blank 100 by spin coating. Next, a second pattern, which is a pattern (light shielding band pattern) to be formed on the light shielding film 3, was exposed and drawn with an electron beam on the resist film, and predetermined treatments such as developing were conducted, to thereby form a second resist pattern 6b having a light shielding pattern (see FIG.7(e)). Subsequently, dry etching was conducted using mixed gas of chlorine-based gas and oxygen gas with the second resist pattern 6b as a mask, and a second pattern (light shielding pattern 3b) was formed on the light shielding film 3 (see FIG.7(f)). Further, the second resist pattern 6b was removed, predetermined treatments such as cleaning were conducted, and the phase shift mask 200 was obtained (see FIG.7(g)).

There is no particular limitation to chlorine-based gas used for the dry etching described above, as long as chlorine(Cl) is included, for example, Cl_2 , SiCl_2 , CHCl_3 , CH_2Cl_2 , CCl_4 , and BCl_3 . Further, there is no particular limitation to fluorine-based gas to be used for the dry etching described above, as long as fluorine(F) is included, for example, CHF_3 , CF_4 , C_2F_6 , C_4F_8 , and SF_6 . Particularly, fluorine-based gas free of carbon(C) can further reduce damage on a glass substrate for having a relatively low etching rate to a glass substrate, and is preferable.

The method for manufacturing a semiconductor device of this invention is characterized in using a transfer mask manufactured by using the mask blank described above, and exposure-transferring a pattern on a resist film on a semiconductor substrate. Therefore, a desired pattern can be transferred to an object to be transferred at a high precision, even if the transfer mask is set on an exposure apparatus and an exposure light is irradiated from the side of the transparent substrate 1 of the transfer mask to perform the exposure-transfer on the object to be transferred (resist film on semiconductor wafer, etc.).

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the art that many variations of the embodiments can be made within the scope and spirit of the present invention.

CLAIMS

1. A method of manufacturing a mask blank comprising a thin film for pattern formation on a substrate, the method comprising:

a step of arranging a target containing one or more elements selected from silicon and metal in a vacuum chamber and forming a thin film by sputtering the target to an atmosphere including noble gas,

wherein a shield is set around the target in the vacuum chamber, the shield being coupled to one or more support members, and

wherein an amount of heat transferred Q from the shield through all of the support members is 100 W or more.

2. The method of manufacturing a mask blank according to claim 1, wherein the amount of heat transferred Q from the shield through all of the support members is 200 W or more.

3. The method of manufacturing a mask blank according to claim 2, wherein the amount of heat transferred Q from the shield through all of the support members is 500 W or more.

4. The method of manufacturing a mask blank according to claim 3, wherein the amount of heat transferred Q from the shield through all of the support members is 800 W or more.

5. The method of manufacturing a mask blank according to any preceding claim, wherein the one or more support members are formed from a material having a thermal conductivity of 50 W/(mm°C) or greater.

6. The method of manufacturing a mask blank according to claim 5, wherein the one or more support members are formed from a material having a thermal conductivity of 100 W/(mm°C) or greater.

7. The method of manufacturing a mask blank according to any preceding claim, wherein the one or more support members are formed from a material comprising one of more of the following: aluminium, cast iron, copper and brass.
8. The method of manufacturing a mask blank according to claim 7, wherein the wherein the one or more support members are formed from a material comprising aluminium.
9. The method of manufacturing a mask blank according any one of the preceding claims, wherein the target contains metal and silicon.
10. The method of manufacturing a mask blank according to any one of the preceding claims, wherein the atmosphere includes noble gas and reactive gas.
11. A method for manufacturing a transfer mask comprising a step of forming a transfer pattern on the thin film of a mask blank manufactured by the method for manufacturing a mask blank according to any one of claims 1 to 10 by dry etching.
12. A method for manufacturing a semiconductor device comprising a step of exposure-transferring a transfer pattern on a resist film on a semiconductor substrate using a transfer mask manufactured by the method for manufacturing a transfer mask according to claim 11.