

DESCRIPTION

Title of the Invention

RESIST LIQUID STORAGE CONTAINER, RESIST LIQUID SUPPLY DEVICE, RESIST LIQUID APPLICATION DEVICE, RESIST LIQUID PRESERVATION DEVICE, AND MASK BLANK MANUFACTURING METHOD

Technical Field

[0001]

This invention relates to a resist liquid storage container configured to store a resist liquid to be used for pattern formation of photolithography, a resist liquid supply device configured to supply the resist liquid from the resist liquid storage container, a resist liquid application device configured to apply the resist liquid onto a substrate or the like after receiving the supply of the resist liquid from the resist liquid supply device, a resist liquid preservation device configured to preserve the resist liquid in the resist liquid storage container in a proper state, and a method of manufacturing a mask blank.

Background Art

[0002]

In manufacturing of semiconductor devices typified by a flat panel display (FPD) and the like, and formation and processing of fine structures such as a magnetic disk and an optical disc, a resist liquid having high sensitivity is used. Further, application of the resist liquid onto a mask blank in a photomask process is performed by a spin coating method. The spin coating method involves setting a target substrate on a spin coater, dropping a predetermined amount of the resist liquid from a nozzle of a resist liquid application device onto the surface of the substrate, and rotating the spin coater

at a high speed, to thereby diffuse and apply the resist liquid onto the substrate.

[0003]

When the resist liquid is in a stationary state, a gel-like undissolved substance is generated in some cases. At the time of diffusing and applying the resist liquid in which the gelled undissolved substance has been generated, when the gelled undissolved substance adheres to the surface of the substrate, the gelled undissolved substance becomes a foreign matter, with the result that a defect occurs in a resist pattern serving as a basis of a fine structure. In order to suppress the generation of the gelled undissolved substance, circulating filtration of the resist liquid is effective. As an example thereof, there has been known a resist liquid supply device in which a circulating filtration device configured to circulate a resist liquid in a bottle-shaped resist liquid storage container formed of glass or the like is incorporated (see, for example, Japanese Unexamined Patent Application Publication (JP-A) No. 2014-63807 (Patent Document 1)).

[0004]

In the resist liquid supply device described in Patent Document 1, when the resist liquid in the bottle-shaped storage container is reduced, a space is formed in an upper part of the storage container. Then, there is a problem in that the resist liquid remaining in the storage container is oxidized with the air having entered the space to change sensitivity.

[0005]

Meanwhile, as a shape of the resist liquid storage container, besides the above-mentioned bottle-shaped container, there have been known a large number of flexible bag-shaped containers formed of a film or the like so that air does not enter the container (see, for example, International Publication No. 1989/07575 (Patent Document 2). Further, there is disclosed a device in which one pipe is inserted into a bag-shaped storage container, and a resist liquid is

introduced from an outside of the container and discharged from the container, to thereby circulate the resist liquid in the storage container (see, for example, Japanese Unexamined Patent Application Publication (JP-A) No. H09-95565 (Patent Document 3)).

Prior Art Documents

Patent Document

[0006]

Patent Document 1: JP-A-2014-63807

Patent Document 2: WO-A1-1989/07575

Patent Document 3: JP-A-H09-95565

Summary of the Invention

Problem to be Solved by the Invention

[0007]

However, the device disclosed in Patent Document 3 described above has the following problem. Specifically, a position of a distal end of the pipe inserted into the container is fixed. Therefore, the resist liquid is constantly introduced into the container from the same position, and further, the resist liquid in the container is constantly discharged from the same position. Thus, the resist liquid in the vicinity of the distal end of the pipe is stirred through movement, but the resist liquid at a position away from the distal end of the pipe is retained without moving. That is, the resist liquid cannot be stirred sufficiently at the position away from the distal end of the pipe, and gelling of the resist liquid in association with a dark reaction occurs.

[0008]

Further, in the device disclosed in Patent Document 3, one pipe is used. Therefore, when the resist liquid is being introduced into the container, the resist

liquid cannot be discharged to the outside from the container. Meanwhile, when the resist liquid is being discharged to the outside from the container, the resist liquid cannot be introduced into the container. That is, a movement direction of the resist liquid in the container is limited to one of the introduction direction and the discharge direction, and hence the resist liquid cannot be stirred efficiently, with the result that there is a risk in that gelling of the resist liquid may occur.

[0009]

This invention has been made so as to solve the above-mentioned problems, and an object of this invention is to provide a flexible resist liquid storage container capable of efficiently circulating a resist liquid in the container, a resist liquid supply device, a resist liquid application device, and a resist liquid preservation device. Another object of this invention is to provide a method of manufacturing a mask blank.

[0010]

In order to resolve the above-mentioned problems, for example, a configuration described in Claims is adopted. A resist liquid storage container according to this invention is a resist liquid storage container configured to store a resist liquid to be used for photolithography, wherein the resist liquid storage container comprises: a flexible bag portion including a receptacle portion configured to store the resist liquid; an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid thereinto; and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the resist liquid storage container.

[0011]

A resist liquid supply device according to this invention comprises: a resist liquid storage container which comprises a flexible bag portion including a

receptacle portion configured to store a resist liquid to be used for photolithography, an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid into the receptacle portion, and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the receptacle portion; a liquid bath configured to immerse the resist liquid storage container with a temperature regulating liquid to be filled into the liquid bath; temperature regulating liquid circulating means for circulating the temperature regulating liquid filled into the liquid bath; temperature control means for controlling a temperature of the filled temperature regulating liquid; and supply means for supplying the resist liquid in the resist liquid storage container to a resist liquid application device.

[0012]

A resist liquid application device according to this invention comprises: a resist liquid storage container which comprises a flexible bag portion including a receptacle portion configured to store a resist liquid to be used for photolithography, an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid into the receptacle portion, and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the receptacle portion; a liquid bath configured to immerse the resist liquid storage container with a temperature regulating liquid to be filled into the liquid bath; temperature regulating liquid circulating means for circulating the temperature regulating liquid filled into the liquid bath; temperature control means for controlling a temperature of the filled temperature regulating liquid; supply means for supplying the resist liquid in the resist liquid storage container to the resist liquid application device; and a dropping nozzle configured to drop the resist liquid, which is supplied by the supply means, onto a surface of a

substrate.

[0013]

A resist liquid preservation device according to this invention comprises: a resist liquid storage container which comprises a flexible bag portion including a receptacle portion configured to store a resist liquid to be used for photolithography, an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid into the receptacle portion, and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the receptacle portion; a liquid bath configured to immerse the resist liquid storage container with a temperature regulating liquid to be filled into the liquid bath; temperature regulating liquid circulating means for circulating the temperature regulating liquid filled into the liquid bath; and temperature control means for controlling a temperature of the filled temperature regulating liquid.

[0014]

A method of manufacturing a mask blank according to this invention comprises the steps of: forming a thin film for mask pattern formation over a surface of a substrate; and applying and fixing a resist liquid onto a surface of the thin film through use of a resist liquid application device, wherein the method comprising the steps of: circulating the resist liquid in a resist liquid storage container in which the resist liquid is stored through use of a discharge tube and an injection tube; circulating a temperature regulating liquid in a bath in which the resist liquid storage container is immersed; controlling a temperature of the temperature regulating liquid in the liquid bath to a temperature suitable for application of the resist liquid; and supplying the resist liquid at the temperature suitable for application of the resist liquid to the resist liquid application device.

Effect of the Invention

[0015]

In the resist liquid storage container according to this invention, the resist liquid stored in the container can be efficiently circulated to suppress gelling of the resist liquid. Further, in the resist liquid storage container according to this invention, even when the resist liquid is stored in an amount equal to or smaller than the capacity of the resist liquid storage container, air and the like can be prevented from entering the container, and a change in sensitivity in association with a dark reaction among resist liquid components, oxygen, and the like can also be effectively suppressed.

[0016]

Further, in the resist liquid supply device according to this invention, the resist liquid can be supplied to the resist liquid application device or the like under a state in which gelling of the resist liquid stored in the resist liquid storage container is suppressed. Further, in the resist liquid supply device according to this invention, air does not enter the resist liquid storage container in place of the supplied resist liquid, and hence a change in resist sensitivity in association with a dark reaction among resist liquid components, oxygen, and the like can also be effectively suppressed.

[0017]

Further, in the resist liquid application device according to this invention, the resist liquid can be applied onto the substrate or the like under a state in which gelling of the resist liquid stored in the resist liquid storage container is suppressed. Thus, in the resist liquid application device according to this invention, an undissolved substance in association with gelling is not generated. Therefore, the undissolved substance is not discharged onto the substrate, and a resist layer containing few foreign matters can be formed. Further, in this application device, air does not enter the resist liquid storage container, and

hence a dark reaction among the resist liquid, the oxygen, and the like can also be suppressed. Thus, in the resist liquid application device according to this invention, the resist liquid excellent in sensitivity stability is constantly supplied onto the substrate, and hence the formed resist layer does not cause a variation in sensitivity on the substrate on a wafer basis.

[0018]

Further, in the resist liquid preservation device according to this invention, the resist liquid can be preserved under a state in which gelling of the resist liquid stored in the resist liquid storage container is suppressed. Air can be prevented from entering between the resist liquid and the storage container, and the change in resist sensitivity in association with a dark reaction can also be effectively suppressed.

[0019]

Further, in the method of manufacturing a mask blank according to this invention, the mask blank can be manufactured through use of the resist liquid in which gelling is suppressed. Therefore, the mask blank including the resist layer having few defects of foreign matters caused by the gelled undissolved substance can be manufactured. Further, in this method, the contact between the resist liquid and the air (oxygen) can be prevented, and hence the mask blank including the resist layer having less fluctuation in sensitivity on a wafer basis can be manufactured.

Brief Description of the Drawings

[0020]

Fig. 1 is a schematic vertical sectional view of a resist liquid storage container according to a first embodiment of this invention.

Fig. 2 is a front view of a holding member of the first embodiment of this invention.

Fig. 3 is a schematic vertical sectional view of a resist liquid storage container according to a second embodiment of this invention.

Fig. 4 is an explanatory view for illustrating a flow of a resist liquid in a receptacle portion of the resist liquid storage container.

Fig. 5 is an explanatory view for illustrating the flow of the resist liquid in the receptacle portion of the resist liquid storage container according to the second embodiment of this invention.

Fig. 6 is a schematic vertical sectional view of a resist liquid storage container according to a third embodiment of this invention.

Fig. 7 is a horizontal sectional view of an injection tube and a discharge tube of the third embodiment of this invention.

Fig. 8 is an explanatory view for illustrating a flow of a resist liquid in a receptacle portion of the resist liquid storage container according to the third embodiment of this invention.

Fig. 9 is a schematic view for illustrating configurations of a resist liquid preservation device, a resist liquid supply device, and a resist liquid application device according to this invention.

Fig. 10 is a graph for showing results of a test for temporal change in sensitivity, which is performed through use of a resist liquid storage container using a flexible bag portion.

Fig. 11 is a step flow diagram of a method of manufacturing a mask blank according to this invention.

Fig. 12A is a schematic sectional view for illustrating one step of manufacturing a phase shift mask.

Fig. 12B is a schematic sectional view for illustrating one step of manufacturing the phase shift mask.

Fig. 12C is a schematic sectional view for illustrating one step of manufacturing the phase shift mask.

Fig. 12D is a schematic sectional view for illustrating one step of manufacturing the phase shift mask.

Fig. 12E is a schematic sectional view for illustrating one step of manufacturing the phase shift mask.

Fig. 12F is a schematic sectional view for illustrating one step of manufacturing the phase shift mask.

Modes for Embodying the Invention

[0021]

Now, modes for carrying out this invention are described with reference to the drawings.

[0022]

[First Embodiment of Resist Liquid Storage Container]

Fig. 1 is a schematic vertical sectional view of a resist liquid storage container 1 according to a first embodiment of this invention, and Fig. 2 is a front view of a holding member 4 of the first embodiment of this invention.

[0023]

<Overall Configuration>

The resist liquid storage container 1 according to the first embodiment includes a bag portion 2 including a receptacle portion 2a configured to store a resist liquid, a mouthpiece member 3 which is arranged in the bag portion 2 and which has an opening 3a that communicates to the receptacle portion 2a, and the holding member 4 fitted with the mouthpiece member 3.

[0024]

<Bag Portion>

In the bag portion 2, the receptacle portion 2a configured to store the resist liquid is formed by superimposing films so that the films are opposed to each other and by heat-sealing four sides of the films. The bag portion 2 is

formed into a rectangular flat shape. Further, each corner portion of the receptacle portion 2a is formed into an arc shape so that the resist liquid is less liable to remain in the corner portion. In the first embodiment, the films are opposed to each other, and the four sides thereof are heat-sealed. However, this invention is not limited thereto. A gusset may be formed in a bottom part of the films. Further, in order to enhance use efficiency of the resist liquid, a bottom side of the bag may be formed into a curved shape or a tapered shape so as to be convex in a bottom direction.

[0025]

As a material for the films, for example, a hydrocarbon-based polymer sheet made of polyethylene, polypropylene, or the like can be used. As a structure of the films, a multilayer film may be used instead of a single layer film. For example, a high-hermetic film configured to block gas, for example, oxygen and water vapor or a functional film having a light shielding property may be separately arranged.

[0026]

<Mouthpiece Member>

The mouthpiece member 3 serving as an engaging and holding portion is a cylindrical member having the opening 3a that communicates to the receptacle portion 2a of the bag portion 2. The opening 3a of the mouthpiece member 3 is engaged with an engaging portion 4b of the holding member 4 when the mouthpiece member 3 and the holding member 4 are fitted with each other. The mouthpiece member 3 is thermally fused to the films in an upper part of the bag portion 2, as illustrated in Fig. 1.

The mouthpiece member 3 is manufactured preferably by an injection molding method. There is no particular limitation on a resin to be used for manufacturing the mouthpiece member 3 as long as the resin can be subjected to injection molding. In general, high-density polyethylene that has stiffness

even at a high temperature and is less liable to be embrittled at a low temperature is preferred.

[0027]

<Holding Member>

The holding member 4 includes a head portion 4a that protrudes to an outside of the bag portion 2 when being fitted with the mouthpiece member 3 and the engaging portion 4b that is inserted into the opening 3a of the mouthpiece member 3 and that has a distal end positioned in the receptacle portion 2a of the bag portion 2. As illustrated in Fig. 1, the opening 3a of the mouthpiece member 3 and the engaging portion 4b of the holding member 4 are engaged with each other, and the holding member 4 is fitted with the mouthpiece member 3.

[0028]

As illustrated in Fig. 2, the head portion 4a of the holding member 4 is formed into a cylindrical shape, and a discharge tube hole 8a into which a discharge tube 8 is inserted is formed in the vicinity of a center of an upper surface 4c of the head portion 4a. The discharge tube hole 8a is formed so as to penetrate through the holding member 4 in an axial direction. Further, the discharge tube hole 8a is formed so that a diameter thereof is slightly smaller than an outer diameter of the discharge tube 8. With this, the discharge tube 8 inserted into the discharge tube hole 8a can be held at a predetermined position, and an inside of the resist liquid storage container 1 can be kept in a liquid-tight state even when the discharge tube 8 is mounted on the holding member 4.

[0029]

An injection tube hole 9a into which an injection tube 9 is inserted is formed in a side peripheral surface 4d of the head portion 4a of the holding member 4. The injection tube hole 9a is formed so as to extend in a direction perpendicular to the axial direction of the holding member 4. Further, the

injection tube hole 9a is formed so that a diameter thereof is slightly smaller than an outer diameter of the injection tube 9. With this, the injection tube 9 inserted into the injection tube hole 9a can be held at a predetermined position, and the inside of the resist liquid storage container 1 can be kept in a liquid-tight state even when the injection tube 9 is mounted on the holding member 4.

[0030]

The engaging portion 4b of the holding member 4 communicates to a lower part of the head portion 4a and is formed into a cylindrical shape having a diameter slightly smaller than that of the head portion 4a. The engaging portion 4b is formed so that an outer diameter thereof is slightly larger than a diameter of the opening 3a of the mouthpiece member 3. With this, when the holding member 4 and the mouthpiece member 3 are fitted with each other, the inside of the resist liquid storage container 1 can be kept in a liquid-tight state. An O-ring may be arranged between the engaging portion 4b and the mouthpiece member 3 to enhance liquid tightness. A step 4e is formed between the head portion 4a and the engaging portion 4b of the holding member 4. When the step 4e is locked onto an edge part of the opening 3a of the mouthpiece member 3, the holding member 4 can be prevented from being pushed into the mouthpiece member 3 more than necessary when the holding member 4 and the mouthpiece member 3 are fitted with each other.

[0031]

A cylindrical space portion 5 is formed in the holding member 4. A lower part of the space portion 5 communicates to the receptacle portion 2a, and an upper part of the space portion 5 communicates to the discharge tube hole 8a and the injection tube hole 9a. Further, the space portion 5 is formed so that a diameter thereof is larger than the outer diameter of the discharge tube 8. With this, even when the discharge tube 8 is mounted on the holding member 4, a gap through which the resist liquid flows is ensured between the

discharge tube 8 and an inner wall of the holding member 4.

[0032]

The holding member 4 is manufactured preferably by the injection molding method. There is no particular limitation on a resin to be used for manufacturing the holding member 4 as long as the resin can be subjected to injection molding. In general, high-density polyethylene that has stiffness even at a high temperature and is less liable to be embrittled at a low temperature is preferred.

[0033]

As illustrated in Fig. 1, the discharge tube 8 is inserted into the discharge tube hole 8a formed in the upper surface 4c of the head portion 4a of the holding member 4 in the axial direction of the holding member 4. The discharge tube 8 is formed of a thin pipe, and a taper 8b is formed in a distal end part of the discharge tube 8. When the taper 8b is formed at the distal end, the resist liquid remaining in the vicinity of a bottom part of the receptacle portion 2a can be discharged even when the distal end of the discharge tube 8 is positioned in the vicinity of a bottom part of the bag portion 2. Another end of the discharge tube 8 is connected to a pump 31 described later.

[0034]

The injection tube 9 is inserted into the injection tube hole 9a formed in the side peripheral surface 4d of the holding member 4 in a direction perpendicular to the axial direction of the holding member 4. The injection tube 9 is formed of a thin pipe and is arranged so that a distal end thereof is positioned before the space portion 5. Specifically, the injection tube 9 communicates to the space portion 5 of the holding member, that is, a space formed between the discharge tube 8 and the inner wall of the holding member 4 without being brought into contact with the discharge tube 8 arranged in the space portion 5. Another end of the injection tube 9 is connected to the pump

31 described later.

[0035]

In the first embodiment, the discharge tube 8 and the injection tube 9 are not required to have a double tube structure by making an insertion direction of the discharge tube 8 mounted on the holding member 4 different from an insertion direction of the injection tube 9 mounted on the holding member 4. With this, the structure of the resist liquid storage container 1 can be simplified.

[0036]

As materials for the discharge tube 8 and the injection tube 9, in general, high-density polyethylene that has stiffness even at a high temperature and that is less liable to be embrittled at a low temperature is preferred. Further, the taper 8b is formed by obliquely cutting the distal end of the discharge tube 8.

[0037]

An inclined part may be formed on the upper surface 4c of the head portion 4a of the holding member 4. With this, when an operation of fitting the holding member 4 and the mouthpiece member 3 with each other through use of a tool, for example, a lever is performed, a part of the tool is allowed to escape in a space portion formed above the inclined part.

[0038]

<Assembly of Resist Liquid Storage Container>

First, a resist liquid is injected through the opening 3a of the mouthpiece member 3 under a state in which the holding member 4 is removed from the mouthpiece member 3 so that the resist liquid is stored in the receptacle portion 2a of the bag portion 2. When the resist liquid storage container 1 is not used immediately, the resist liquid storage container 1 is stored under a state in which the opening 3a of the mouthpiece member 3 is closed. As the resist liquid to be injected, a resist liquid having high sensitivity, in particular, a

chemically-amplified resist liquid may be used besides a general resist liquid. The resist liquid storage container 1 according to the first embodiment includes the flexible bag portion 2 in which air does not enter the receptacle portion 2a. Therefore, the chemically-amplified resist liquid that is easily oxidized with air can also be stored.

[0039]

When the resist liquid storage container 1 is used, the stopper of the opening 3a is removed, and the holding member 4 having the discharge tube 8 and the injection tube 9 mounted thereon is fitted with the mouthpiece member 3. In this case, the distal end of the discharge tube 8 is inserted into the receptacle portion 2a from the opening 3a, and then, the engaging portion 4b of the holding member 4 is engaged with the opening 3a of the mouthpiece member 3, to thereby assemble the resist liquid storage container 1. At this time, the discharge tube 8 is mounted on the holding member 4 so that the distal end of the discharge tube 8 is positioned in the vicinity of the bottom part of the bag portion 2. The position of the distal end of the discharge tube 8 in the receptacle portion 2a may be defined by bending a part of the discharge tube 8 and locking the bent part onto an edge part of the discharge tube hole 8a of the holding member 4. With this, it is possible to prevent the distal end of the discharge tube 8 from being inserted excessively deeply to damage the bag portion 2 and the distal end of the discharge tube 8 from being inserted excessively shallowly to cause the resist liquid to remain in the receptacle portion 2a.

[0040]

The resist liquid storage container 1 assembled as illustrated in Fig. 1 is set in a resist liquid supply device, a resist liquid application device, and a resist liquid preservation device described later.

[0041]

When the resist liquid stored in the receptacle portion 2a is circulated, the resist liquid is discharged from a distal end of the injection tube 9. The resist liquid discharged from the distal end of the injection tube 9 passes through the space portion 5 formed in the holding member 4 and moves to the receptacle portion 2a of the bag portion 2. Then, the resist liquid is sucked into the discharge tube 8 from the distal end of the discharge tube 8 and is discharged to an outside of the resist liquid storage container 1. Thus, along with the movement of the resist liquid in which the resist liquid injected through the injection tube 9 is discharged to an outside of the storage container 1 through the discharge tube 8, the resist liquid stored in the receptacle portion 2a is agitated. Thus, through use of the resist liquid storage container 1 according to the first embodiment, the resist liquid is not retained in the receptacle portion 2a, and hence gelling of the resist liquid in association with a dark reaction can be suppressed.

[0042]

[Second Embodiment of Resist Liquid Storage Container]

Next, a resist liquid storage container 11 according to a second embodiment of this invention will be described. The resist liquid storage container 11 according to the second embodiment is different from the first embodiment in arrangement of the discharge tube 8 and the injection tube 9 mounted on the holding member 4. The entire configuration of the resist liquid storage container 11 according to the second embodiment is the same as that of the first embodiment, and hence description thereof is omitted. Further, in Fig. 3, parts corresponding to those of Fig. 1 are denoted by the same reference symbols, and overlapping description is omitted.

[0043]

Fig. 3 is a schematic vertical sectional view of the resist liquid storage container 11 according to the second embodiment of this invention. Fig. 4 and

Fig. 5 are explanatory views for illustrating a flow of the resist liquid in the receptacle portion 2a of the resist liquid storage container 11.

[0044]

As illustrated in Fig. 3, the discharge tube 8 and the injection tube 9 are mounted on the holding member 4 so as to be parallel to each other in the axial direction of the holding member 4. The distal ends of the discharge tube 8 and the injection tube 9 mounted on the holding member 4 are arranged so as to be positioned in the receptacle portion 2a. The discharge tube hole 8a and the injection tube hole 9a are formed in the upper surface 4c of the head portion 4a of the holding member 4 of the second embodiment, and the discharge tube hole 8a and the injection tube hole 9a are formed so as to penetrate through the holding member 4 in the axial direction.

[0045]

The second embodiment is different from the above-mentioned first embodiment in that the distal end of the injection tube 9 is also arranged so as to be positioned in the receptacle portion 2a. Specifically, the distal end of the injection tube 9 is arranged so as to be in the vicinity of the opening 3a of the mouthpiece member 3. In the same manner as in the first embodiment, the distal end of the discharge tube 8 inserted into the receptacle portion 2a is arranged so as to be positioned in the vicinity of the bottom part of the receptacle portion 2a. Thus, the distal end of the injection tube 9 inserted into the receptacle portion 2a is arranged so as to be positioned above the distal end of the discharge tube 8.

[0046]

In the second embodiment, in the receptacle portion 2a, the position of the distal end of the discharge tube 8 and the position of the distal end of the injection tube 9 are separated in a vertical direction with the position of the distal end of the injection tube 9 being in the upper position. With this, a movement

distance in which the resist liquid injected from the distal end of the injection tube 9 moves to the distal end of the discharge tube 8 becomes long, and the resist liquid in the receptacle portion 2a can be reliably agitated. Further, the movement of the resist liquid injected through the injection tube 9 can be performed smoothly utilizing gravity by setting the distal end of the injection tube 9 in the upper position, and hence the resist liquid in the receptacle portion 2a can be reliably agitated.

[0047]

In the second embodiment, when the resist liquid stored in the receptacle portion 2a is circulated, the resist liquid is directly injected from the distal end of the injection tube 9 into the receptacle portion 2a of the bag portion 2 and discharged to an outside of the container 11 from the distal end of the discharge tube 8. In the second embodiment, the resist liquid in the receptacle portion 2a is agitated along with the movement of the resist liquid, and hence gelling of the resist liquid in association with a dark reaction can be suppressed.

[0048]

Fig. 4 is a view for illustrating an embodiment in the case where the distal ends of the discharge tube 8 and the injection tube 9 are arranged at the same height in the receptacle portion 2a. In a resist liquid storage container 11' according to this embodiment, the distal ends of the discharge tube 8 and the injection tube 9 are arranged in the vicinity of the bottom part of the receptacle portion 2a. In this figure, there is illustrated a state in which air in the receptacle portion 2a is discharged to the outside of the container along with reduction in resist liquid in the receptacle portion 2a to cause the flexible bag portion 2 to shrink, with the result that the space in which the resist liquid can move in the receptacle portion 2a is decreased. As a result of the decrease in space in which the resist liquid can move, the resist liquid in the vicinity of the distal end of the discharge tube 8 and the resist liquid in the vicinity of the distal

end of the injection tube 9 are separated from each other to generate a so-called liquid pool Q in the receptacle portion 2a. When the liquid pool Q is generated as described above, the resist liquid in the receptacle portion 2a cannot be circulated in some cases.

[0049]

Fig. 5 is a view for illustrating the circulation of the resist liquid in the case where the remaining amount of the resist liquid in the receptacle portion 2a has been decreased in the resist liquid storage container 11 illustrated in Fig. 3.

As illustrated in Fig. 5, when the flexible bag portion 2 shrinks, the space in which the resist liquid can move is decreased. Therefore, the liquid pool Q is generated in the vicinity of the distal end of the injection tube 9. However, in this embodiment, an end of the liquid pool Q is brought into contact with an outer peripheral surface of the discharge tube 8, the liquid pool Q is guided to the discharge tube 8 to reach the distal end of the discharge tube 8 due to gravity. The resist liquid having reached the distal end of the discharge tube 8 is discharged to the outside of the container 11. Thus, through use of the resist liquid storage container 11 according to this embodiment, the resist liquid in the receptacle portion 2a can be reliably circulated even when the resist liquid in the receptacle portion 2a is decreased to cause a state in which the liquid pool Q is liable to be generated. With this, gelling of the resist liquid in association with a dark reaction can be suppressed.

[0050]

[Third Embodiment of Resist Liquid Storage Container]

Next, a resist liquid storage container 21 according to a third embodiment of this invention will be described. The resist liquid storage container 21 according to the third embodiment is different from the first embodiment in arrangement of the discharge tube 8 and the injection tube 9

mounted on the holding member 4, and has a double tube structure. The entire configuration of the resist liquid storage container 21 according to the third embodiment is the same as that of the first embodiment, and hence description thereof is omitted. Further, in Fig. 6, parts corresponding to those of Fig. 1 are denoted by the same reference symbols, and overlapping description is omitted.

[0051]

Fig. 6 is a schematic vertical sectional view of the resist liquid storage container 21 according to the third embodiment of this invention. Fig. 7 is a horizontal sectional view of the discharge tube 8 and the injection tube 9 taken along the line A-A of Fig. 6, and Fig. 8 is an explanatory view for illustrating a flow of the resist liquid in the receptacle portion 2a of the resist liquid storage container 21.

[0052]

As illustrated in Fig. 6, the resist liquid storage container 21 according to the third embodiment has the so-called double tube structure in which a diameter of the injection tube 9 is larger than that of the discharge tube 8, and the discharge tube 8 is arranged on an inner side of the injection tube 9. The discharge tube 8 and the injection tube 9, which form the double tube structure, are inserted into a through hole 9b formed in the upper surface 4c of the head portion 4a of the holding member 4. The through hole 9b is formed so as to have a diameter slightly smaller than the outer diameter of the injection tube 9 so that the through hole 9b penetrates through the holding member 4 in the axial direction.

[0053]

As illustrated in Fig. 7, the discharge tube 8 and the injection tube 9, which form the double tube structure, have a common concentric axis, and a space portion 10 through which the resist liquid injected through the injection

tube 9 passes is formed between an outer peripheral surface of the discharge tube 8 and an inner peripheral surface of the injection tube 9.

[0054]

Further, the distal end of the discharge tube 8 inserted into the receptacle portion 2a is arranged so as to be positioned in the vicinity of the bottom part of the receptacle portion 2a, and the distal end of the injection tube 9 inserted into the receptacle portion 2a is arranged so as to be positioned above the distal end of the discharge tube 8. Specifically, the distal end of the injection tube 9 is arranged so as to protrude from the opening 3a of the mouthpiece member 3 to be positioned in the receptacle portion 2a. The distal end of the injection tube 9 may be positioned in the through hole 9b of the holding member 4.

[0055]

Fig. 8 is a view for illustrating the circulation of the resist liquid in the case where the remaining amount of the resist liquid in the receptacle portion 2a has been decreased in the resist liquid storage container 1 illustrated in Fig. 6.

As illustrated in Fig. 8, when the remaining amount of the resist liquid in the receptacle portion 2a has been decreased, the resist liquid injected from the distal end of the injection tube 9 moves along the outer peripheral surface of the discharge tube 8 arranged on an inner side of the double tube structure to reach the vicinity of the distal end of the discharge tube 8. That is, a liquid pool is not generated in the vicinity of the distal end of the injection tube 9. The resist liquid having reached the distal end of the discharge tube 8 is discharged to an outside of the storage container 21 through the discharge tube 8. Thus, in the resist liquid storage container 21 according to the third embodiment, even when the remaining amount of the resist liquid in the receptacle portion 2a is decreased to cause a state in which a liquid pool is liable to be generated in the

receptacle portion 2a, the resist liquid can be circulated in the receptacle portion 2a without generating a liquid pool in the vicinity of the distal end of the injection tube 9. With this, gelling of the resist liquid in association with a dark reaction can be suppressed.

[0056]

As described above, the resist liquid storage container of this invention includes the flexible bag portion 2 formed of a film in any of the embodiments.

Now, comparison was made between a resist liquid storage container using a flexible bag portion and a resist liquid storage container using a non-flexible bottle as a bag portion by a test for temporal change in sensitivity.

[0057]

<Sensitivity Change with Time Test>

[Example 1]

A resist liquid storage container using a flexible bag portion formed of a film was manufactured.

[0058]

[Comparative Example 1]

A resist liquid storage container using a non-flexible glass bottle as a bag portion was manufactured.

[0059]

Each of the resist liquid storage containers manufactured as described above was stored in an environment at a temperature of 10°C and evaluated by performing a test one week, two weeks, one month, two months, and three months after the commencement of the storage.

A resist layer was formed on a substrate through use of a resist liquid stored in the resist liquid storage container and evaluated for sensitivity by measuring a critical dimension uniformity (CDU). The results thereof are shown in Fig. 10.

The resist layer used for evaluation was formed under the condition of a pre-exposure baking at 190°C, a film pressure of 60 seconds, and a film thickness of 120 nm through use of a chemically-amplified positive resist (PRL009S manufactured by FUJIFILM Electronic Materials Co., Ltd.) as a resist liquid.

[0060]

As is apparent from Fig. 10, it is understood that the resist liquid storage container of Example 1 can keep a value of CDU at a high state as compared to the resist liquid storage container of Comparative Example 1. It is understood from the foregoing that, through use of the flexible bag portion as in the resist liquid storage container according to any of the embodiments, the contact of air with the resist liquid during storage can be suppressed to reduce degradation in sensitivity of the resist liquid with time.

[0061]

As described above, in the resist liquid storage container according to this invention, the resist liquid stored in the receptacle portion 2a is circulated in any of the embodiments.

Now, comparison was made between a resist liquid storage container in which the resist liquid stored in the receptacle portion is circulated and a resist liquid storage container in which the resist liquid stored in the receptacle portion is not circulated by a foreign matter test.

[0062]

<Foreign Matter Test>

[Example 2]

A resist liquid storage container including a bag portion formed of a film was used in a resist liquid supply device described later and stored for 24 hours while circulating filtration was performed.

[0063]

[Comparative Example 2]

A resist liquid storage container including a bag portion formed of a film was used in a resist liquid supply device and stored for 24 hours while circulation was not performed.

[0064]

After that, a resist layer was formed on a substrate through use of a resist liquid stored in the resist liquid storage container, and evaluation of counting the number of defects in the resist layer, which were caused by gelling of the resist liquid, was performed five times. The forming condition of the resist layer was set to be the same as that in the case of the test for temporal change in sensitivity.

A filter was set in the discharge tube in the case of Comparative Example 2.

[0065]

As a result, in the case of Example 2, no defects having a depth of 0.2 μm or more were counted in any of the evaluations. However, in the case of Comparative Example 2, defects having a depth of 0.2 μm or more were counted in eleven portions on an average.

[0066]

It is understood from the above-mentioned results that, in the case of Example 2, gelled foreign matters were not generated in the resist liquid in the receptacle portion as compared to the case of Comparative Example 2. It is understood from the results of Comparative Example 2 that gelled foreign matters generated in the resist liquid cannot be completely removed even through use of the filter. It is understood from the foregoing that, when the resist liquid stored in the container is circulated as in the resist liquid storage container according to any of the embodiments, gelling of the resist liquid in association with a dark reaction can be suppressed to suppress the generation

of gelled foreign matters in the resist liquid during storage.

[0067]

[Embodiments of Resist Liquid Supply Device, Resist Liquid Application Device, and Resist Liquid Preservation Device]

Now, embodiments of a resist liquid supply device, a resist liquid application device, and a resist liquid preservation device, which use the resist liquid storage container 1 according to this invention, will be described with reference to the drawings.

[0068]

Fig. 9 is a schematic view for illustrating configurations of a resist liquid supply device 80, a resist liquid application device 90, and the resist liquid preservation device according to this invention. In Fig. 9, a main body of the resist liquid supply device 80 is illustrated in a partially cutaway sectional view, and a configuration of a fluid control system is illustrated in a fluid circuit diagram. Further, the resist liquid application device 90 includes a dropping nozzle 20 configured to drop a resist liquid onto a surface of a target substrate S, for example, a photomask blank set on a spin coater 41.

[0069]

The resist liquid supply device 80 includes the resist liquid storage container 1 configured to store a resist liquid in a liquid state and a liquid bath 12 configured to immerse the resist liquid storage container 1 stored therein with a filled temperature regulating liquid 14. The resist liquid storage container 1 may be stored in the resist liquid supply device 80 under a state in which the resist liquid storage container 1 is received in an external container formed into a cylindrical shape.

[0070]

An inner wall defining an internal space of the liquid bath 12 has a cylindrical shape, and the resist liquid storage container 1 is stored in the

internal space. By forming the inner wall of the liquid bath 12 into a cylindrical shape, a circulating flow of the temperature regulating liquid 14 can be formed or accelerated even when the rectangular resist liquid storage container 1 is stored. Although not shown, a window portion enabling visual measurement of the amount of the resist liquid in the resist liquid storage container 1 may be arranged in a part of the liquid bath 12.

[0071]

The liquid bath 12 is formed with liquid tightness so that the temperature regulating liquid 14 can be filled up to a predetermined height. Further, the liquid bath 12 includes an upper lid 18 in which the holding member 4 of the resist liquid storage container 1 can be fitted, and thus the temperature regulating liquid 14 is prevented from scattering. In this case, the resist liquid storage container 1 is mounted on the upper lid 18 under a state in which the bag portion 2 is not floated even when the resist liquid stored in the receptacle portion 2a is decreased. Although pure water can be used as the temperature regulating liquid 14, the temperature regulating liquid 14 may be a water solution obtained by adding an evaporation inhibitor, for example, ethylene glycol to pure water in order to stabilize the liquid amount.

[0072]

The temperature regulating liquid 14 is supplied into the liquid bath 12 through a water supply line 16 in advance. Further, the temperature regulating liquid 14 filled into the liquid bath 12 can also be discharged through a water discharge line 17. In the liquid tank 12, the temperature regulating liquid 14 is filled up to a water level higher than a level of the resist liquid in the resist liquid storage container 1 set at a predetermined position. With this, the resist liquid storage container 1 is immersed with the temperature regulating liquid 14.

[0073]

The resist liquid supply device 80 includes resist liquid supply means 30

for supplying the resist liquid in the resist liquid storage container 1 to the resist liquid application device 90. The resist liquid supply means 30 includes, at least, the pump 31 for resist liquid supply, a main body discharge tube 32 which is connected between the resist liquid storage container 1 and an intake side of the pump 31 and which is configured to suck up the resist liquid in the resist liquid storage container 1 with a negative pressure generated by the pump 31, and a supply tube 33 which is connected to a discharge side of the pump 31 and which is configured to supply the resist liquid discharged from the pump 31 to the resist liquid application device 90 (dropping nozzle 20). A distal end of the main body discharge tube 32 is connected to the discharge tube 8 mounted on the resist liquid storage container 1. As the discharge tube 8, the main body discharge tube 32 may be directly mounted on the holding member 4 of the resist liquid storage container 1.

[0074]

It is preferred that the pump 31 be a rotary pump which has a constant discharge flow rate of the resist liquid and which generates extremely less cavitation (air bubbles). Further, a filter 34 configured to filtrate and remove particles or gelled components that may be contained in the resist liquid may be arranged on a discharge side pipe of the pump 31 as illustrated in Fig. 9. Although not shown, such filter may be arranged on an intake side pipe of the pump 31. Further, such filter may be arranged in the middle of a pipeline in which the resist liquid is circulated by resist liquid circulating means 70 described later.

[0075]

The liquid bath 12 includes temperature regulating liquid circulating means 40 for circulating the temperature regulating liquid 14 in the liquid bath 12 and temperature control means 50 for adjusting the temperature regulating liquid 14 in the liquid bath 12 to an appropriate temperature. With the

temperature regulating liquid circulating means 40 and the temperature control means 50, the temperature regulating liquid 14 can be kept in a constant state, and the resist liquid in the resist liquid storage container 1 can be prevented from having a local temperature difference.

[0076]

Further, the resist liquid supply device 80 includes the resist liquid circulating means 70 for circulating the resist liquid in the resist liquid storage container 1. In Fig. 9, the resist liquid circulating means 70 includes the pump 31, the main body discharge tube 32 which is connected to an intake port of the pump 31 and which has a suction port side inserted into the resist liquid storage container 1, and a return tube 36 which is branched through a three-way valve 35 from the supply tube 33 connected to a discharge port of the pump 31 and which has an injection port side inserted into the resist liquid storage container 1. The return tube 36 includes a deaeration device 42 configured to remove air accumulated in the main body discharge tube 32 and the return tube 36 to the outside. A distal end of the return tube 36 is connected to the injection tube 9 mounted on the resist liquid storage container 1. As the injection tube 9, the return tube 36 may be directly mounted on the holding member 4 of the resist liquid storage container 1.

[0077]

The resist liquid circulating means 70 functions when the communication of the three-way valve 35 is switched to the return tube 36 side. When the resist liquid is supplied to the resist liquid application device 90, the communication of the three-way valve 35 is switched to the supply tube 33 side. The three-way valve 35 may comprise an electromagnetic valve, and such switching of an operation mode of supply/circulation of the resist liquid may be automatically controlled with programming. Further, such switching may be manually performed as needed through use of the three-way valve 35 of a

manual operation type.

[0078]

In the resist liquid supply device 80 according to this embodiment, the resist liquid stored in the receptacle portion 2a of the resist liquid storage container 1 can be circulated to be supplied to the resist liquid application device 90 and the like. Thus, gelling of the resist liquid in the resist liquid storage container 1 can be suppressed, and the resist liquid containing few gelled foreign matters can be supplied to the resist liquid application device 90 and the like. Further, in the resist liquid application device 90 according to this embodiment, the resist liquid can be applied onto a substrate or the like through use of the resist liquid containing no gelled foreign matters.

[0079]

The resist liquid supply device 80 having the above-mentioned configuration also serves as a resist liquid preservation device configured to preserve the resist liquid in a proper state. In this case, the resist liquid preservation device includes the resist liquid storage container 1 configured to store the resist liquid, the liquid bath 12 configured to immerse the resist liquid storage container 1 with the temperature regulating liquid 14, the temperature regulating liquid circulating means 40 for circulating the temperature regulating liquid 14, and the temperature control means 50 for controlling the temperature of the temperature regulating liquid 14.

[0080]

In the resist liquid preservation device, the temperature of the resist liquid stored in the resist liquid storage container 1 can be set to a proper state by controlling the temperature of the temperature regulating liquid 14 with the temperature control means 50. It is preferred that the temperature range of the temperature regulating liquid 14 controlled with the temperature control means 50 includes, at least, a first temperature (for example, a room temperature of

23°C) suitable for application of the resist liquid and a second temperature (for example, a cool temperature of 10°C) suitable for storage of the resist liquid.

[0081]

With this, during a non-application period, the resist liquid can be stored while maintaining the second temperature (cold temperature). For example, when a chemically-amplified resist having sensitivity that changes significantly at a room temperature is used, the accumulation time during which the resist liquid is placed in a room temperature environment can be reduced to suppress the degradation in sensitivity of the resist liquid. Further, in the resist liquid preservation device according to this embodiment, the resist liquid stored in the receptacle portion 2a of the resist liquid storage container 1 can be preserved in a circulated state. Thus, gelling of the resist liquid in the resist liquid storage container 1 can be suppressed, and the resist liquid can be preserved under a state in which the generation of gelled foreign matters was suppressed.

[0082]

[Embodiment of Method of Manufacturing Mask Blank]

Next, an embodiment of a method of manufacturing a mask blank according to this invention will be described.

[0083]

A mask blank is manufactured in accordance with, for example, a step flow illustrated in Fig. 11.

[0084]

First, a surface of a mask blank substrate S is polished to provide high flatness having a surface roughness of 1 nm or less (Step S1). A light shielding film made of a metal thin film of Cr or the like is formed on the polished surface of the substrate S (Sep S2). As a film forming method for the light shielding film, a vacuum vapor deposition method, a sputtering method, or the like can be used.

[0085]

Prior to the step of resist application by the resist liquid application device 90, the resist liquid supply device 80 is set up. For example, as illustrated in Fig. 9, the resist liquid supply device 80 includes the resist liquid storage container 1 configured to store the resist liquid, the supply means 30 for supplying the resist liquid in the resist liquid storage container 1 to the dropping nozzle 20, the liquid bath 12 configured to immerse the resist liquid storage container 1 with the temperature regulating liquid 14 to be filled into the liquid bath 12, the temperature regulating liquid circulating means 40 for circulating the temperature regulating liquid 14, and the temperature control means 50 for controlling the temperature of the temperature regulating liquid 14.

[0086]

In preparation of the resist liquid supply device 80, the resist liquid storage container 1 configured to store the resist liquid is immersed in the liquid bath 12 into which the temperature regulating liquid 14 is filled. Then, the temperature regulating liquid circulating means 40 is operated to circulate the temperature regulating liquid 14 in the liquid bath 12 (Step S3).

[0087]

Simultaneously with the foregoing, the temperature control means 50 is operated to control the temperature of the temperature regulating liquid 14 to be circulated in the liquid bath 12 to a temperature (for example, a room temperature of 23°C) suitable for application of the resist liquid (Step S4).

[0088]

Next, the resist liquid is supplied from the resist liquid supply device 80 to the resist liquid application device 90 by the supply means 30 (Step S5). Then, only a predetermined amount of the resist liquid is dropped onto the mask blank substrate S mounted on the spin coater 41 from the dropping nozzle 20.

The resist liquid is diffused to be uniformly applied onto the surface of the mask blank substrate S by rotating the spin coater 41 at a high speed (Step S6).

[0089]

Then, the mask blank substrate S having the resist liquid applied thereto is transferred to a hot plate device and is baked while keeping the surface temperature of the mask blank substrate S at about 100°C (Step S7). With this, an organic solvent contained in the resist liquid is evaporated, and the resist is fixed onto the mask blank substrate S.

[0090]

[Example]

In Example, a mask blank substrate (transparent substrate) made of an alloy quartz glass having main surface dimensions of about 152 mm x about 152 mm and a thickness of about 6.25 mm was prepared. The end surface and the main surface of the mask blank substrate were polished to a predetermined surface roughness, and then, the mask blank substrate was subjected to predetermined cleaning treatment and drying treatment.

[0091]

Next, a halftone-type phase shift film (thin film for pattern formation) made of nitrided molybdenum and silicon was formed on the above-mentioned mask blank substrate.

[0092]

Specifically, the mask blank substrate was set in a sheet-type DC sputtering device, and a MoSiN film made of molybdenum, silicon, and nitrogen was formed to a film thickness of 69 nm by reactive sputtering (DC sputtering) at a gas pressure of 0.3 Pa and an electric power of a DC power source of 3.0 kW in a mixed gas atmosphere of argon (Ar), nitrogen (N₂), and helium (He) (gas flow ratio of Ar:N₂:He=5:49:46) through use of a mixed target of molybdenum (Mo) and silicon (Si) (Mo:Si=10 at%:90 at%).

[0093]

Then, the substrate having the above-mentioned MoSiN film formed thereon was subjected to heating processing as annealing treatment. Specifically, the heating processing was performed at a heating temperature of 450°C for a heating time of 1 hour in the atmosphere through use of a heating furnace. The MoSiN film had a transmittance of 6.16% and a phase difference of 184.4° in an ArF excimer laser.

[0094]

Next, a light shielding film (thin film for pattern formation) made of a chromium-based material was formed on the halftone-type phase shift film.

Specifically, a CrOCN film was formed to a film thickness of 30 nm by reactive sputtering (DC sputtering) at a gas pressure of 0.2 Pa and an electric power of a DC power source of 1.7 kW in a mixed gas atmosphere of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (gas flow ratio of Ar:CO₂:N₂:He=20:35:10:30) through use a chromium (Cr) target.

[0095]

Subsequently, a CrN film was formed to a film thickness of 4 nm by reactive sputtering (DC sputtering) at a gas pressure of 0.1 Pa and an electric power of a DC power source of 1.7 kW in a mixed gas atmosphere of argon (Ar) and nitrogen (N₂) (gas flow ratio of Ar:N₂=25:75) through use a chromium (Cr) target.

[0096]

Further, a CrOCN film was formed to a film thickness of 14 nm by reactive sputtering (DC sputtering) at a gas pressure of 0.2 Pa and an electric power of a DC power source of 1.7 kW in a mixed gas atmosphere of argon (Ar), carbon dioxide (CO₂), nitrogen (N₂), and helium (He) (gas flow ratio of Ar:CO₂:N₂:He=20:35:5:30) through use a chromium (Cr) target.

[0097]

Through the above-mentioned procedure, a light shielding film (film thickness: 48 nm) of a chromium-based material having a three-layer laminate structure of a CrOCN film, a CrN film, and a CrOCN film was formed from the substrate side in the stated order. Through the above-mentioned steps, a halftone-type phase shift mask blank (mask blank) was obtained. The mask blank of Example had an optical density (OD) of 3.0 with respect to an ArF excimer laser (wavelength: 193 nm) and a surface reflectance of the light shielding film of 20%.

[0098]

In the method of manufacturing a resist mask according to this embodiment, the resist liquid in the resist liquid storage container 1 is circulated to suppress gelling of the resist liquid in association with a dark reaction, and the resist liquid containing few gelled foreign matters is used. Therefore, a mask blank having less defects can be manufactured. In this embodiment, a substrate for a photomask was used as a substrate onto which the resist liquid was applied, but a substrate for an imprint may be applied.

[0099]

<Manufacturing of Halftone-type Phase Shift Mask>

Next, a phase shift mask 150 was manufactured through use of the mask blank manufactured by the above-mentioned method. Fig. 12A to Fig. 12F are each a schematic sectional view for illustrating a step of manufacturing the phase shift mask 150 through use of a phase shift mask blank 100. First, a resist film 104 was formed on the mask blank 100 through use of the resist liquid application device 90 (see Fig. 12A).

[0100]

Next, the resist film 104 formed on the mask blank 100 was subjected to pattern lithography of a phase shift pattern through use of an electron beam lithography apparatus. After that, the resultant was developed with a

predetermined developer to form a resist pattern 104a (see Fig. 12B).

[0101]

Next, a light shielding film 103 (Cr-based light shielding film) was etched through use of the resist pattern 104a as a mask to form a light shielding film pattern 103a (see Fig. 12C). As a dry etching gas, a mixed gas of Cl_2 and O_2 was used.

[0102]

Next, the halftone-type phase shift film 102 (MoSiN film) was etched through use of the light shielding film pattern 103a as a mask to form a phase shift pattern 102a (see Fig. 12D). As a dry etching gas, a mixed gas of SF_6 and He was used.

[0103]

Next, the resist film 104 was similarly formed on the mask blank 100 and subjected to pattern lithography of a light shielding band through use of the electron beam lithography apparatus. After that, the resultant was developed with a predetermined developer to form a resist pattern 104b (see Fig. 12E).

[0104]

Next, the light shielding film pattern 103a (Cr-based light shielding film) was etched through use of the resist pattern 104b as a mask to form a light shielding film pattern (light shielding band) 103b. As a dry etching gas, a mixed gas of Cl_2 and O_2 was used.

[0105]

Next, the remaining resist pattern was peeled to obtain the phase shift mask 150 (see Fig. 12F). In this embodiment, the mask blank 100 having less defects is used as described above, and hence the high-quality phase shift mask 150 can be obtained.

[0106]

This invention is described above with reference to the embodiments.

However, this invention is not limited to the configurations described in the above-mentioned embodiments, and the configurations can be modified suitably without departing from the spirit of this invention. For instance, the embodiments described above are detailed descriptions written for an easy understanding of this invention, and this invention is not necessarily limited to a configuration that includes all of the described components. Further, the configuration of one embodiment may partially be replaced by the configuration of another embodiment. The configuration of one embodiment may be joined by the configuration of another embodiment. A part of the configuration of the embodiment may have another configuration added thereto or removed therefrom, or may be replaced by another configuration.

This application is based upon and claims the benefit of priority from Japanese Patent Application No. 2015-063639, filed on March 26, 2015, the disclosure of which is incorporated herein in its entirety by reference.

Reference Signs List

[0107]

1, 11, 11', 21 ... resist liquid storage container, 2 ... bag portion, 2a ... receptacle portion, 3 ... mouthpiece member, 4 ... holding member, 8 ... discharge tube, 9 ... injection tube, 80 ... resist liquid supply device (resist liquid preservation device), 90 ... resist liquid application device, 40 ... temperature regulating liquid circulating means, 50 ... temperature control means, 100 ... mask blank

CLAIMS

1. A resist liquid storage container configured to store a resist liquid to be used for photolithography, comprising:

a flexible bag portion including a receptacle portion configured to store the resist liquid;

an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid into the receptacle portion; and

a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the resist liquid storage container.

2. A resist liquid storage container according to claim 1, further comprising a holding member configured to hold the injection tube and the discharge tube,

wherein the holding member is mounted on the bag portion under a state in which the injection tube and the discharge tube communicate to the receptacle portion.

3. A resist liquid storage container according to claim 2, comprising, in the bag portion, an engaging and holding portion configured to mount the holding member on the bag portion through engagement with the holding member.

4. A resist liquid storage container according to claim 2, wherein the holding member has a cylindrical shape including an upper surface portion and a side surface portion,

wherein the injection tube is held by the upper surface portion, and

wherein the discharge tube is held by the side surface portion.

5. A resist liquid storage container according to claim 2, wherein the injection tube in the receptacle portion has a distal end arranged so as to be positioned on the holding member side from a distal end of the discharge tube.

6. A resist liquid storage container according to any one of claims 1 to 5,

wherein the injection tube and the discharge tube are arranged so that a center axis of the injection tube and a center axis of the discharge tube are matched with each other, and

wherein the injection tube has a diameter larger than that of the discharge tube.

7. A resist liquid supply device, comprising:

a resist liquid storage container which comprises a flexible bag portion including a receptacle portion configured to store a resist liquid to be used for photolithography, an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid into the receptacle portion, and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the receptacle portion;

a liquid bath configured to immerse the resist liquid storage container with a temperature regulating liquid to be filled into the liquid bath;

temperature regulating liquid circulating means for circulating the temperature regulating liquid filled into the liquid bath;

temperature control means for controlling a temperature of the filled temperature regulating liquid; and

supply means for supplying the resist liquid in the resist liquid storage container to a resist liquid application device.

8. A resist liquid application device, comprising:

a resist liquid storage container which comprises a flexible bag portion including a receptacle portion configured to store a resist liquid to be used for photolithography, an injection tube configured to communicate to the receptacle

portion and configured to inject the resist liquid into the receptacle portion, and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the receptacle portion;

a liquid bath configured to immerse the resist liquid storage container with a temperature regulating liquid to be filled into the liquid bath;

temperature regulating liquid circulating means for circulating the temperature regulating liquid filled into the liquid bath;

temperature control means for controlling a temperature of the filled temperature regulating liquid;

supply means for supplying the resist liquid in the resist liquid storage container to the resist liquid application device; and

a dropping nozzle configured to drop the resist liquid, which is supplied by the supply means, onto a surface of a substrate.

9. A resist liquid preservation device, comprising:

a resist liquid storage container which comprises a flexible bag portion including a receptacle portion configured to store a resist liquid to be used for photolithography, an injection tube configured to communicate to the receptacle portion and configured to inject the resist liquid into the receptacle portion, and a discharge tube configured to communicate to the receptacle portion and configured to discharge the resist liquid stored in the receptacle portion to an outside of the receptacle portion;

a liquid bath configured to immerse the resist liquid storage container with a temperature regulating liquid to be filled into the liquid bath;

temperature regulating liquid circulating means for circulating the temperature regulating liquid filled into the liquid bath; and

temperature control means for controlling a temperature of the filled temperature regulating liquid.

10. A method of manufacturing a mask blank, comprising the steps of:
forming a thin film for pattern formation over a surface of a substrate;
and
applying and fixing a resist liquid onto a surface of the thin film through
use of a resist liquid application device,
wherein the method comprising the steps of:
circulating the resist liquid in a resist liquid storage container in which
the resist liquid is stored through use of a discharge tube and an injection tube;
circulating a temperature regulating liquid in a bath in which the resist
liquid storage container is immersed;
controlling a temperature of the temperature regulating liquid in the bath
to a temperature suitable for application of the resist liquid; and
supplying the resist liquid at the temperature suitable for application of
the resist liquid to the resist liquid application device.