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 liquid 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.

When the resist liquid stored in the receptacle portion 2a is circulated, the resist liquid is injected from a distal end of the injection tube 9. The resist liquid injected 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

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 a comparative example 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 comparative example, 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 second 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 second 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 central axis, and a space portion 10 through which the resist liquid injected through the injection

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 with the pump 31 side via 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 with the pump 31 side via 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

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 Resist Film Coated Mask Blank]

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

[0083]

A resist film coated 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.

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. Thus, the resist film coated mask blank is manufactured.

[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 (N_2), and helium (He) (gas flow ratio of Ar:N_2:He=5:49:46) through use of a mixed target of molybdenum (Mo) and silicon (Si) (Mo:Si=10 at%:90 at%).

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) 100 (see, Fig. 12A) was obtained. The mask blank 100 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 film coated mask blank 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 resist film coated mask blank having less defects can be manufactured. In this Example, a mask blank substrate 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 (see, the above-mentioned Example). 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 (see, the above-mentioned Example). First, a resist film 104 was formed on the mask blank 100 through use of the resist liquid application device 90 (see Fig. 12A) to obtain the resist film coated mask blank (see, Fig. 11).

[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 resist film coated mask blank (Fig. 12A) 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.

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 liquid 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.