

DESCRIPTION

TITLE OF THE INVENTION:

ULTRASONIC CLEANING HEAD, SUBSTRATE CLEANING METHOD,
5 SUBSTRATE CLEANING DEVICE, METHOD FOR MANUFACTURING
SUBSTRATE, AND METHOD FOR MANUFACTURING MASK BLANK
FOR EUVL

TECHNICAL FIELD

10 [0001] The disclosures herein relate to an
ultrasonic cleaning head, a substrate cleaning method,
a substrate cleaning device, a method for
manufacturing substrate, and a method for
manufacturing mask blank for EUVL.

15 BACKGROUND ART

[0002] In recent years, as semiconductor devices
are refined, EUV lithography (EUVL), which is an
exposure technology using Extreme Ultra-Violet (EUV),
has been developed. EUV, which includes soft X-ray
20 and vacuum ultra-violet, specifically, is a light
with a wavelength of about 0.2 nm-100 nm. At the
present time, EUV with a wavelength of about 13.5 nm
is mainly examined.

[0003] In EUVL, a reflective mask is used. The
25 reflective mask includes a substrate such as a glass
substrate, a multi-layer reflective film which
reflects EUV, and an absorbing film which absorbs EUV
in this order. Opening patterns are made in the
absorbing film. In EUVL, the opening patterns of the
30 absorbing film are copied on target substrates such
as semiconductor substrates. Copying includes
reduced-size copying.

[0004] During a manufacturing process of a mask

blank for EUVL, the glass substrate or functional films formed on the glass substrate may be cleaned. As one of cleaning methods, ultrasonic cleaning may be conducted.

5 [0005] The cleaning method described in PTL 1 includes spraying cleaning liquid, to which ultrasound is applied in advance, from a nozzle to the upper surface of the rotating substrate. In the cleaning method described in PTL 2, the upper surface
10 of the substrate is cleaned by supplying cleaning liquid between the rotating upper surface of the substrate and the lower surface of an ultrasonic cleaning head, and applying ultrasound to the cleaning liquid from the lower surface of the
15 ultrasonic cleaning head.

CITATION LIST

PATENT LITERATURE

[0006] PTL 1: Japanese Laid-Open Patent
20 Publication No. 2013-158664
PTL 2: Japanese Laid-Open Patent
Publication No. 2001-87725

SUMMARY OF THE INVENTION

25 PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] Even if the cleaning method disclosed in PTL 1 is performed, it is not possible to reduce a number of particles adhered to a substrate efficiently. As the present inventors researched on
30 the particles adhered to the substrate after ultrasonic cleaning, it was determined that cerium oxide particles are one of causes of the particles. Moreover, as an origin of the cerium oxide particles,

it was determined that the cerium oxide particles adhered to an ultrasonic cleaning head are separated during cleaning and adhere to the substrate. Since cerium oxide particles are generally used for
5 mechanical polishing, it is supposed that they adhered during manufacturing processes of the ultrasonic cleaning head. Manufacturing processes include, for example, cutting and mechanical polishing. In a cutting process, a diaphragm is cut
10 into a desired shape. In a mechanical polishing process, the diaphragm is polished with cerium oxide particles.

[0008] One embodiment of the present disclosure provides technologies to reduce the number of
15 particles that adhere to a substrate by an ultrasonic cleaning.

MEANS OF SOLVING THE PROBLEM

[0009] An ultrasonic cleaning head related to one
20 embodiment of the present disclosure has a vibration surface that faces the upper surface of a substrate with a gap therebetween, and comes in contact with a liquid film formed on the upper surface of the substrate. The vibration surface has a surface
25 density of Ce element of 30×10^{10} atoms/cm² or less as detected by a total reflection X-ray fluorescence analysis.

EFFECTS OF THE INVENTION

30 [0010] As an ultrasonic cleaning head of one embodiment of the present disclosure has a vibration surface with a surface density of Ce element of 30×10^{10} atoms/cm² or less, a surface density of cerium

oxide particles that adhere to the vibration surface is low. Therefore, the number of particles that separate from the vibration surface of the ultrasonic cleaning head can be reduced, and the number of particles that adhere to a substrate by ultrasonic cleaning can be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] [Fig. 1] Fig. 1 is a side view illustrating a substrate cleaning apparatus related to one embodiment.

[Fig. 2] Fig. 2 is a cross section illustrating one example of an inner structure of a cleaning head.

[Fig. 3] Fig. 3 is a cross section illustrating another example of an inner structure of a cleaning head.

[Fig. 4] Fig. 4 is a plan view illustrating one example of a movement track of a cleaning head.

[Fig. 5] Fig. 5 is a cross section illustrating one example of a pretreatment of a cleaning head.

[Fig. 6] Fig. 6 is a cross section illustrating another example of a pretreatment of a cleaning head.

[Fig. 7] Fig. 7 is a drawing illustrating one example of a relationship between a number of treated dummy substrates and a number of particles.

[Fig. 8] A flow chart illustrating a method for manufacturing a mask blank for EUVL related to one embodiment.

[Fig. 9] Fig. 9 is a cross section

illustrating one example of a substrate.

[Fig. 10] Fig. 10 is a plan view of the substrate drawn in Fig. 9.

[Fig. 11] Fig. 11 is a cross section of one
5 example of a mask blank for EUVL.

[Fig. 12] Fig. 12 is a cross section of an example of a mask for EUVL.

MODES FOR CARRYING OUT THE INVENTION

10 [0012] Hereinafter, modes for carrying out the invention will be described with reference to the drawings. In the drawings, the same constituent elements are denoted with the same reference numerals, and redundant description thereabout may be omitted.
15 In this description, a mark "-" showing a number range means that the numbers next to the mark are included in the range as the lowest and the highest values.

[0013] A substrate cleaning apparatus 1 relating to one embodiment will be described with reference to
20 Fig. 1 to Fig. 4. The substrate cleaning apparatus 1 cleans a substrate W by applying ultrasonic vibration to a liquid film F formed on the substrate W. Particles adhered to the substrate W can be removed. The substrate cleaning apparatus 1 includes a
25 retaining part 10, a nozzle 20, a cleaning head 30, a rotating part 40, a first movement part 50, a second movement part 60, and a control part 90. The cleaning head 30 is one example of an ultrasonic cleaning head.

[0014] The retaining part 10 retains the substrate
30 W horizontally. Seen from above, the substrate W is rectangular (see Fig. 4), but it may be circular. The substrate W may be a glass substrate, a silicon wafer, or a compound semiconductor wafer. The substrate W

may include functional films formed on a glass substrate, etc. The functional films are, for example, a light reflective film, a light absorbing film, an electroconductive film, an insulating film, etc.

5 [0015] The retaining part 10, as shown in Fig. 1, includes a plurality of pins 11 spaced apart along a peripheral edge of the substrate W. The plurality of pins 11 support the peripheral edge of the substrate W. The substrate W is placed on the plurality of pins
10 11. Since there is a gap under the substrate W, a sensor can be set under the substrate W. Moreover, the retaining part 10 may hold the substrate W by a vacuum grip.

[0016] The nozzle 20 forms the liquid film F by
15 supplying cleaning liquid to the upper surface Wa of the substrate W retained with the retaining part 10. The upper surface Wa of the substrate W is also referred to as the substrate upper surface Wa. The nozzle 20 supplies the cleaning liquid, for example,
20 to around the center of the substrate upper surface Wa. As the substrate W is rotating, the cleaning liquid on the substrate W is spread by centrifugal force from the center of the substrate W to the peripheral edge. As a result, the liquid film F is
25 formed on the whole of the substrate upper surface Wa. The nozzle 20 may be installed outside the cleaning head 30 as shown in Fig. 1, or inside the cleaning head 30, although not shown.

[0017] The nozzle 20 is connected to a supply 22
30 of the cleaning liquid through a supply line 21. A valve 23 is installed partway on the supply line 21. The valve 23 opens and closes a channel of the supply line 21. When the valve 23 opens the channel of the

supply line 21, the cleaning liquid is supplied from the supply 22 to the nozzle 20, and the nozzle 20 discharges the cleaning liquid. When the valve 23 closes the channel of the supply line 21, the nozzle
5 20 stops discharging the cleaning liquid.

[0018] The cleaning liquid is, for example, pure water (e.g., deionized water), a mixture of pure water and X (at least one selected from a group consisting of hydrochloric acid, sulfuric acid, nitric acid,
10 phosphoric acid, formic acid, and acetic acid), a mixture of pure water and Y (at least one selected from a group consisting of ammonia, tetramethylammonium hydroxide, triethanolamine, choline, sodium hydroxide, potassium hydroxide, and
15 cesium hydroxide), a mixture of pure water and Z (at least one selected from a group consisting of hydrogen peroxide, perchloric acid ion, and periodic acid ion), a mixture of pure water, X, and Z, or a mixture of pure water, Y, and Z.

20 [0019] The cleaning liquid may contain at least one dissolved gas selected from a group consisting of H₂ gas, CO₂ gas, N₂ gas, O₂ gas, O₃ gas, and Ar gas. By controlling dissolved gas amount, cavitation occurrence efficiency can be improved, and particle
25 removal efficiency can be improved. Gas dissolved in the cleaning liquid is favorably H₂ gas, CO₂ gas, or N₂ gas, and more favorably CO₂ gas.

[0020] The cleaning head 30 includes, as shown in Fig. 2, a vibration surface 31a is in contact with
30 the liquid film F, and an ultrasonic transducer 32 which vibrates the vibration surface 31a. The cleaning head 30 includes a diaphragm 31. The diaphragm 31 includes the vibration surface 31a,

which is the lower surface to come in contact with the liquid film F, and an attachment surface 31b, which is the upper surface to attach the ultrasonic transducer 32.

5 [0021] The vibration surface 31a is installed parallel to the substrate upper surface Wa. The size of the vibration surface 31a is smaller than that of, for example, the substrate upper surface Wa. The shape of the vibration surface 31a is, for example, circular.
10 Moreover, when the nozzle 20 is installed inside the cleaning head 30, a discharge opening of the nozzle 20 is formed on the vibration surface 31a.

[0022] The attachment side 31b may be installed parallel to the vibration surface 31a as shown in Fig. 2, and may also be installed obliquely to the vibration surface 31a as shown in Fig. 3. In Fig. 3, θ is an angle between a normal to the vibration surface 31a and a normal to the attachment side 31b. The direction of the normal to the attachment side
15 31b is a direction of vibration of the ultrasonic transducer 32.
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[0023] The ultrasonic transducer 32 applies ultrasonic vibration to the liquid film F by vibrating the vibration surface 31a and applying sound pressure to the substrate W. By this means, particles adhered
25 to the substrate upper surface Wa can be removed. Output of the ultrasonic transducer 32 is controlled by the control part 90. When the distance D between the cleaning head 30 and the substrate W is constant, the higher the output PW of the ultrasonic transducer
30 32 is, the higher sound pressure SP acting on the substrate W becomes.

[0024] A rotating part 40 rotates the substrate W

along with the retaining part 10. A rotational axis 10R of the retaining part 10 is installed vertically. The retaining part 10 retains the substrate W in order for the rotational axis 10R to locate the center of the substrate W. The rotating part 40 includes a servomotor 41. Rotary driving force of the servomotor 41 may be transmitted to the retaining part 10 through pulleys, belts or gears, not shown. The servomotor 41 transmits information about rotary position of the retaining part 10 to the control part 90. The rotary position of the retaining part 10 is described by rotation angle. A stepping motor may be used instead of the servomotor 41.

[0025] The first movement part 50 moves the cleaning head 30 horizontally in the direction perpendicular to the rotational axis 10R of the retaining part 10. The cleaning head 30 is moved, for example, between right above the center of the substrate W and right above the peripheral edge of the substrate W. The first movement part 50 includes, for example, a servomotor 51. The servomotor 51 transmits information about horizontal position of the cleaning head 30 to the control part 90. A stepping motor may be used instead of the servomotor 51.

[0026] The first movement part 50 moves the cleaning head 30 horizontally in the direction perpendicular to the rotational axis 10R of the retaining part 10, for example, by rotating a pivot 52. The pivot 52 is fixed to one end of a rotation arm 53, and the cleaning head 30 is fixed to the other end of the rotation arm 53. A rotational axis 30R of the cleaning head 30 is installed vertically.

[0027] Although not shown, moreover, the first movement part 50 may move the cleaning head 30 horizontally in the direction perpendicular to the rotational axis 10R of the retaining part 10 along a horizontal guide rail.

[0028] The second movement part 60 moves the cleaning head 30 vertically. For example, the second movement part 60 moves the cleaning head 30 vertically by moving the pivot 52 vertically. The second movement part 60 includes a servomotor 61. The second movement part 60 may include, for example, a ball screw which converts rotary motion of the servomotor 61 into linear motion. The servomotor 61 transmits information about horizontal position of the cleaning head 30 to the control part 90. A stepping motor may be used instead of the servomotor 61. The second movement part 60 may move the cleaning head 30 vertically by an air cylinder instead of a motor.

[0029] Although not shown, moreover, the second movement part 60 may move the retaining part 10 vertically instead of moving the cleaning head 30 vertically. In either event, the distance D between the substrate W and the cleaning head 30 can be changed.

[0030] The control part 90 controls the valve 23, the ultrasonic transducer 32, the rotating part 40, the first movement part 50, and the second movement part 60. The control part 90 is, for example, a computer, which includes a CPU (Central Processing Unit) 91 and the storage 92 such as a memory. The storage 92 stores programs to control various processes perform in the substrate cleaning apparatus 1. The control part 90 controls the movement of the

substrate cleaning apparatus 1 by making the CPU 91 execute the programs stored in the storage 92.

[0031] Next, a movement of the substrate cleaning apparatus 1, i.e., a substrate cleaning method is described. First, a conveyor robot, not shown, enters the inside of the substrate cleaning apparatus 1, and passes the substrate W to the retaining part 10. After the retaining part 10 has retained the substrate W horizontally, the conveyor robot exits from the substrate cleaning apparatus 1. This is how the substrate W is carried in.

[0032] Next, the rotating part 40 rotates the substrate W with the retaining part 10, and the nozzle 20 supplies the cleaning liquid to around the center of the substrate W. The cleaning liquid on the substrate W is spread by centrifugal force from the center of the substrate W to the peripheral edge. As a result, the liquid film F is formed on the whole of the substrate upper surface Wa. A supply of the cleaning liquid is, for example, 0.1 L/min-5.0 L/min, preferably 0.8 L/min-1.6 L/min.

[0033] Next, in order for the vibration surface 31a of the cleaning head 30 to contact the liquid film F, the first movement part 50 adjusts a horizontal position of the cleaning head 30, and the second movement part 60 adjusts a vertical position of the cleaning head 30. Between the cleaning head 30 and the substrate W, a desired space is formed. The length of the space is, for example, 0.1 mm-5.0 mm, preferably 1.0 mm-4.0 mm.

[0034] Next, the ultrasonic transducer 32 vibrates the vibration surface 31a of the cleaning head 30, to apply ultrasonic vibration to the liquid film F, and

to apply sound pressure to the substrate upper surface Wa.

[0035] Next, the first movement part 50 moves the cleaning head 30 in a horizontal direction perpendicular to the rotational axis 10R of the retaining part 10. The cleaning head 30 is reciprocated between the position right above the center of the substrate W and the position right above the peripheral edge of the substrate W. The substrate W rotating, the whole of the substrate upper surface Wa is cleaned.

[0036] Next, after the second movement part 60 has lifted the cleaning head 30, the first movement part 50 moves the cleaning head 30 horizontally to a standby position. Seen from above, the standby position is located outside the peripheral edge of the substrate W. Moreover, the ultrasonic transducer 32 stops the vibration of the vibration surface 31a, and the nozzle 20 stops supplying the cleaning liquid.

[0037] Next, with the nozzle 20 stopping supplying the cleaning liquid, by the rotating part 40 rotating the substrate W with the retaining part 10, the cleaning liquid on the substrate W is swung away from the peripheral edge of the substrate W by centrifugal force. The liquid film F is removed from the substrate W, and the substrate W is dried.

[0038] Next, the conveyor robot, not shown, enters the inside of the substrate cleaning apparatus 1, and receives the substrate W from the retaining part 10. After the conveyor robot has retained the substrate W, the conveyor robot gets out from the substrate cleaning apparatus 1. This is how the substrate W is carried out.

[0039] Next, referring to Fig. 5 and Fig. 6, one example of a pretreatment of the cleaning head 30 is described. The pretreatment of the cleaning head 30 is performed before the cleaning head 30 is installed in the substrate cleaning apparatus 1. After the cleaning head 30 is installed in the substrate cleaning apparatus 1, the substrate cleaning apparatus cleans a dummy substrate, and then it cleans the substrate W, which is a product. Moreover, the pretreatment of the cleaning head 30 may be performed before the cleaning of the dummy substrate, and can be performed after the installation of the cleaning head 30 in the substrate cleaning apparatus 1.

[0040] A dummy substrate is constituted same as the substrate W, which is a product, and cleaned same as the substrate W. Specifically, although not shown, the dummy substrate is cleaned by forming a liquid film F between the vibration surface 31a of the cleaning head 30 and the upper surface of the dummy substrate, which are opposite each other, and applying ultrasonic vibration from the vibration surface 31a to the liquid film F. The cleaning of the dummy substrate is referred to as dummy cleaning hereinafter. Dummy cleaning is performed in order to prevent dust from the cleaning head 30.

[0041] As shown in Fig. 5 and Fig. 6, particles P adhere to the vibration surface 31a of the cleaning head 30. A distance between the vibration surface 31a of the cleaning head 30 and the upper surface of the dummy substrate is short, and particles P separated from the vibration surface 31a of the cleaning head 30 tend to adhere to the upper surface of the dummy substrate. Moreover, it is in practice difficult to

make the number of the particles P to adhere zero.

[0042] Dummy cleaning is performed repeatedly, changing dummy substrates. As shown in Fig. 7, the more dummy substrates are treated, that is, the longer
5 the dummy cleaning time, as dust from the cleaning head 30 is prevented, the less the particles P adhere to a dummy substrate by ultrasonic cleaning.

[0043] As shown in Fig. 7, as the dummy cleaning time reaches a certain length, a number of the
10 particles P to adhere to a dummy substrate stabilizes to a certain amount. Then, the substrate W, which is a product, is cleaned. The particles P to adhere to the substrate W are as many as the particles P to adhere to the last dummy substrate.

15 [0044] Note that, the fewer the particles P to adhere to the vibration surface 31a of the cleaning head 30 before the dummy cleaning, not only the shorter the time to stabilize the number of the particles P to a certain amount, but also the smaller
20 the certain amount is. Therefore, the fewer the particles P to adhere to the vibration surface 31a of the cleaning head 30, the less the particles P adhere to the substrate W.

[0045] The present inventors examined the cause of
25 the adherence of the particle P to the vibration surface 31a of the cleaning head 30. The particles P are assumed to adhere during any of a manufacturing, a packing, or a transporting process of the cleaning head 30. The present inventors focused on cerium oxide
30 particles used during the manufacturing process of the cleaning head 30.

[0046] The vibration surface 31a of the cleaning head 30 is, as shown in Fig. 2 and Fig. 3, formed on

the diaphragm 31. Material of the diaphragm 31 is, for example, quartz glass (SiO_2). Moreover, material of the diaphragm 31 may be sapphire glass (Al_2O_3). Moreover, material of the diaphragm 31 may be either
5 crystalline or amorphous.

[0047] The manufacturing process of the cleaning head 30 includes, for example, cutting and mechanical polishing. In a cutting process, the diaphragm 31 is cut into a desired shape. In a mechanical polishing
10 process, the diaphragm 31 is polished with cerium oxide particles after the cutting process. It is assumed that cerium oxide particles adhere to the diaphragm 31 during the mechanical polishing process. Moreover, the manufacturing process of the cleaning
15 head 30 may include, for example, a flame polishing process between the cutting process and the mechanical polishing process.

[0048] The present inventors examined removing cerium oxide particles that adhere to the diaphragm
20 31 by supplying at least one of the first chemical liquid L1 and the second chemical liquid L2, described below, to the diaphragm 31 before the dummy cleaning. Removing the cerium oxide particles enables not only to shorten the time to stabilize the number of the
25 particles P to a certain amount, but also to reduce the certain amount.

[0049] The first chemical liquid L1 removes the cerium oxide particles by dissolving the cerium oxide particles that adhere to the diaphragm 31. The first
30 chemical liquid L1 is, although not limited specifically as long as it dissolves cerium oxide, for example, a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) (what is called SPM), or a

water solution including sulfuric acid. The first chemical liquid L1 may be heated in order to promote dissolving of cerium oxide.

[0050] The first chemical liquid L1 is, for example as shown in Fig. 5, stored in a first chemical liquid tank 101. By dipping the diaphragm 31 into the first chemical liquid L1 stored in the first chemical liquid tank 101, the first chemical liquid L1 is supplied to the diaphragm 31. Moreover, a supplying method of the first chemical liquid L1 is not specifically limited. For example, the first chemical liquid L1 may be sprayed on the diaphragm 31.

[0051] The second chemical liquid L2 separates cerium oxide particles from the diaphragm 31 by dissolving the surface of the diaphragm 31. The second chemical liquid L2 is selected suitably for the material of the diaphragm 31, for example, a water solution including hydrofluoric acid (HF), or a water solution including alkaline cleaner. The water solution including alkaline cleaner is preferably that of pH 9 or more. If pH is 9 or more, a Si-O bond can be broken, and SiO₂ can be etched. The alkaline cleaner includes, for example NaOH or KOH. The second chemical liquid L2 may be heated in order to promote dissolving of the cleaning head 30.

[0052] The second chemical liquid L2 is, for example as shown in Fig. 6, stored in a second chemical liquid tank 102. By dipping the diaphragm 31 into the second chemical liquid L2 stored in the second chemical liquid tank 102, the second chemical liquid L2 is supplied to the diaphragm 31. Moreover, a supplying method of the second chemical liquid L2 is not specifically limited. For example, the second

chemical liquid L2 may be sprayed on the diaphragm 31.

[0053] The first chemical liquid L1 and the second chemical liquid L2 may be supplied not only to the vibration surface 31a of the diaphragm 31, but also to the lateral surface 31c. Moreover, although not shown, when the discharge opening of the nozzle 20 is formed on the vibration surface 31a of the diaphragm 31, it is preferable to supply the first chemical liquid L1 and the second chemical liquid L2 to the inside of the nozzle 20. It is preferable to supply the first chemical liquid L1 and the second chemical liquid L2 to a part of the diaphragm 31 to come in contact with the cleaning liquid.

[0054] Only one of either the first chemical liquid L1 or the second chemical liquid L2 may be used, but it is preferable to use both of them. When both the first chemical liquid L1 and the second chemical liquid L2 are used, it is preferable to supply the second chemical liquid L2 to the diaphragm 31 after supplying the first chemical liquid L1 to the diaphragm 31.

[0055] When the second chemical liquid L2 is supplied to the diaphragm 31 after the first chemical liquid L1 is supplied to the diaphragm 31, compared with the case of the opposite order, surface roughness of the diaphragm 31 is further prevented. Because if the surface of the diaphragm 31 is dissolved after the particles P that adhere to the surface of the diaphragm 31 are dissolved, the surface of the diaphragm 31 is dissolved evenly.

[0056] After supplying an acidic chemical liquid as the first chemical liquid L1 or the second chemical

liquid L2 to the diaphragm 31, it is preferable to supply an alkaline chemical liquid to the diaphragm 31. The alkaline chemical liquid can control the zeta potential of both the cleaning head 30 and the particles P to be of the same polarity (e.g., negative), and prevent the particles P from adhering again. The alkaline chemical liquid is, for example, a water solution including an alkaline cleaner, or a mixture of ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2) (what is called SC-1).

[0057] After supplying the first chemical liquid L1 and the second chemical liquid L2 to the diaphragm 31, it is preferable to supply a rinsing liquid to the diaphragm 31 to remove remaining chemical liquid. As the rinsing liquid, pure water such as DIW (deionized water) is used.

[0058] Moreover, cerium oxide particles can be separated from the diaphragm 31 by dry etching the surface of the diaphragm 31. For dry etching of the diaphragm 31, for example, a fluorine plasma is used.

[0059] The number of cerium oxide particles that adhere to the vibration surface 31a of the cleaning head 30 can be represented by the surface density of Ce element detected by a total reflection X-ray fluorescence (TXRF) method of the vibration surface 31a. The lower the surface density of the Ce element is, the fewer cerium oxide particles there are.

[0060] The present inventors found that ultrasonic cleaning can reduce the particles P that adhere to the substrate W, if the surface density of Ce element detected by the TXRF method of the vibration surface 31a of the cleaning head 30 is reduced to 30×10^{10} atoms/cm² or less by chemical liquid, described in

detail in the Examples section.

[0061] If the surface density of Ce element of the vibration surface 31a of the cleaning head 30 is 30×10^{10} atoms/cm² or less, the surface density of the cerium oxide particles that adhere to the vibration surface 31a is low. Therefore, the particles P that separate from the vibration surface 31a of the cleaning head 30 can be reduced, and the particles P that adhere to the substrate W by ultrasonic cleaning can be reduced.

[0062] Moreover, there is no limitation to supply at least one of the first chemical liquid L1 and the second chemical liquid L2 to the diaphragm 31 to reduce the surface density of Ce element of the vibration surface 31a of the cleaning head 30 to 30×10^{10} atoms/cm² or less. For example, the density of cerium oxide particles may be reduced to the value within the designated range by scrubbing with a brush or a sponge.

[0063] The surface density of Ce element of the vibration surface 31a of the cleaning head 30 is, from the perspective of reducing the particles P that adhere to the substrate W by the ultrasonic cleaning, preferably 10×10^{10} atoms/cm² or less, and more preferably 1×10^{10} atoms/cm² or less. The surface density of Ce element of the vibration surface 31a of the cleaning head 30 may be 0 atoms/cm² or more.

[0064] In the vibration surface 31a of the cleaning head 30, when surface density of a most prevalent element among elements of atomic numbers 13-30 and 33-72 detected by the TXRF method is regarded as 100%, a sum of surface densities of all the elements except for the most prevalent element is

preferably 1.0% or less. When the material of the vibration surface 31a is SiO_2 , the most prevalent element is Si. When the material of the vibration surface 31a is Al_2O_3 , the most prevalent element is Al. Moreover, the atomic number of Ce is 58.

[0065] The element of atomic number 13 is Al. The element of atomic number 30 is Zn. The element of atomic number 33 is As. The element of atomic number 72 is Hf. It is assumed here to use a W (tungsten) beam as X-ray source of the TXRF method. When W beam is used, it is difficult to detect Ga, whose atomic number is 31, and Ge, whose atomic number is 32.

[0066] When the sum of surface densities of all elements except for the most prevalent element is 1.0% or less, there are few particles P that adhere to the vibration surface 31a. Therefore, the particles P to separate from the vibration surface 31a of the cleaning head 30 can be reduced, and the particles P to adhere to the substrate W by the ultrasonic cleaning can be reduced.

[0067] The sum of surface densities of all elements except the most prevalent element is, from the perspective of reducing the particles P to adhere to the substrate W, preferably 0.5% or less. Although the total surface density of all elements except the most prevalent element, may be 0.0% or more, from the perspective of productivity, it is preferably 0.1% or more.

[0068] Next, referring to Fig. 8, a method for manufacturing a mask blank for EUVL 200 shown in Fig. 11 is described. The method for manufacturing a mask blank for EUVL 200 includes steps S101-S107. For example, a substrate 210 shown in Fig. 9 or Fig. 10

is prepared in advance. The steps S101-S104 are included in the substrate manufacturing method.

[0069] The substrate 210 includes a first main surface 211 and a second main surface 212 facing an opposite direction to the first main surface. 211 The first main surface 211 is rectangular. In the present disclosure, a rectangular shape includes a shape with chamfered corners. Moreover, a rectangle includes a square. The second main surface 212 faces the opposite direction to the first main surface 211. The second main surface 212 is also rectangular, same as the first main surface 211.

[0070] Moreover, the substrate 210 includes four end surfaces 213, four first chamfered surfaces 214, and four second chamfered surfaces 215. The end surface 213 is perpendicular to the first main surface 211 and the second main surface 212. The first chamfered surface 214 is formed on the border between the first main surface 211 and the end surface 213. The second chamfered surface 215 is formed on the border between the second main surface 212 and the end surface 213. In the present embodiment, the first chamfered surface 214 and the second chamfered surface 215 are what are called C chamfered faces, but they may also be R chamfered faces.

[0071] The substrate 210 is, for example a glass substrate. Glass for the substrate 210 is preferably quartz glass including TiO_2 . Compared with general soda-lime glass, quartz glass has a higher coefficient of linear expansion, and its size changes less by change of temperature. The quartz glass may include 80-95 mass% of SiO_2 , and 4-17 mass% of TiO_2 . When a content of TiO_2 is 4-17 mass%, the coefficient

of linear expansion around room temperature is near zero, and the size changes little around room temperature. The quartz glass may include a third component other than SiO_2 and TiO_2 or impurities.

- 5 [0072] The size of the substrate 210 is, in planar view, for example 152 mm long and 152 mm wide. The length and the width may also be greater than 152 mm.
- [0073] The substrate 210 includes a central region 211A and a peripheral region 211B in the first main
10 substrate 211. The central region 211A is a square region except for the frame-shaped peripheral region 211B, which surrounds the central region 211A, a region which is processed to desired flatness through the steps S101-S104, and a quality guaranteed region.
- 15 The quality guaranteed region is, for example 142 mm long and 142 mm wide. Four edges of the central region 211A are parallel to the four end surfaces 213. The center of the central region 211A matches the center of the first main surface 211.
- 20 [0074] Moreover, although not shown, the second main surface 212 of the substrate 210 also has a central region and a peripheral region same as the first surface 211. The central region of the second main surface 212 is a square region same as the
- 25 central region of the first main surface 211, a region processed to desired flatness through the steps S101-S104 of Fig. 8, and a quality guaranteed region. The quality guaranteed region is, for example 142 mm long and 142 mm wide.
- 30 [0075] The step S101 includes polishing the first main substrate 211 and the second main substrate 212 of the substrate 210. In the present embodiment, the first main substrate 211 and the second main substrate

212 are polished simultaneously by a not shown double-sided polisher, but may be polished alternately by a not shown single-sided polisher. In the step S101, the substrate 210 is polished while polishing slurry is supplied between the polishing pad and the substrate 210.

[0076] As a polishing pad, for example, a polyurethane polishing pad, a nonwoven fabric polishing pad, or a suede polishing pad is used. The polishing slurry includes abrasives and a dispersion medium. Abrasives are, for example cerium oxide particles. A dispersion medium is, for example water or an organic solvent. The first main surface 211 and the second main surface 212 may be polished by abrasives of different materials or sizes for a plurality of times.

[0077] Moreover, abrasives used in the step S101 are not limited to cerium oxide particles, and may also be, for example, silicon oxide particles, aluminum oxide particles, zirconium oxide particles, titanium oxide particles, diamond particles, silicon carbide particles, etc.

[0078] The step S102 includes measurement of surface morphology of the first main surface 211 and the second main surface 212 of the substrate 210. In order to measure the surface morphology, in order not to damage the surface, for example, a non-contact approach, such as from a laser interferometric measuring apparatus is used. The measuring apparatus measures surface morphology of the central region 211A of the first main surface 211, and the central region of the second main surface 212.

[0079] The step S103 includes local treatment of

the first main surface 211 and the second main surface 212 of the substrate 210, referring to the result of the measurement in the step S102. The first main surface 211 and the second main surface 212 are partially polished alternately. Whichever surface may be polished first, and the order is not limited.

[0080] For the local treatment, at least one selected from, for example, GCIB (Gas Cluster Ion beam) method, PCVM (Plasma Chemical Vaporization Machining) method, a polishing method using a magnetic fluid, and a polishing method using a rotational polishing tool, is used.

[0081] The step S104 includes the final polishing of the first main surface 211 and the second main surface 212 of the substrate 210. The first main surface 211 and the second main surface 212 are polished simultaneously by a not shown double-sided polisher, but may be polished alternately by a not shown single-sided polisher. In the step S104, the substrate 210 is polished while polishing slurry is supplied between the polishing pad and the substrate 210. The polishing slurry includes abrasives. The abrasives are, for example, colloidal silica particles.

[0082] The step S105 includes forming an electroconductive film 240 shown in Fig. 11 on the central region of the second main surface 212 of the substrate 210. The electroconductive film 240 is used to hold the mask for EUVL to an electrostatic chuck of an exposure apparatus. The electroconductive film 240 is formed from, for example chromium nitride (CrN), etc. As the electroconductive film 240 forming method, for example sputtering is used.

[0083] The step S106 includes forming a multi-layer reflective film 220 shown in Fig. 11 on the central region 211A of the first main surface 211 of the substrate 210. The multi-layer reflective film 220 reflects EUV. The multi-layer reflective film 220 is formed, for example, by stacking highly refractive layers and low refractive layers alternately. The highly refractive layer is formed from, for example silicon (Si), and the low refractive layer is formed from, for example molybdenum (Mo). As the multi-layer reflective film 220 forming method, for example, sputtering methods such as an ion beam sputtering method, and a magnetron sputtering method are used.

[0084] The step S107 includes forming an absorbing film 230 shown in Fig. 11 on the multi-layer reflective film 220 formed in the step S106. The absorbing film 230 absorbs EUV. The absorbing film 230 may be a phase shift film, and the phase of the EUV may be shifted. The absorbing film 230 is formed from a single metal including at least one element selected from tantalum (Ta), chromium (Cr), and palladium (Pd), alloy, a nitride, an oxide, an oxynitride, etc. As the absorbing film 230 forming method, for example a sputtering method is used.

[0085] Moreover, in the present embodiment, the steps S106-S107 are performed after the step S105, but they may be performed before the step S105.

[0086] By the steps S101-S107 above, the mask blank for EUVL 200 shown in Fig. 11 is obtained. The mask blank for EUVL 200 includes the electroconductive film 240, substrate 210, multi-layer reflective film 220, and the absorbing film 230, in this order. Moreover, the mask blank for EUVL 200

may contain other films adding to the electroconductive film 240, substrate 210, multi-layer reflective film 220, and the absorbing film 230. [0087] For example, the mask blank for EUVL 200 may include, moreover, a low reflective film. The low reflective film is formed on the absorbing film 230. Then, opening patterns 231 are formed in both the low reflective film and the absorbing film 230. The low reflective film is used for an inspection of the opening patterns 231, and has lower reflectance properties against the inspection light than the absorbing film 230. The low reflective film is formed from, for example TaON, TaO, etc. As the low reflective film forming method, for example a sputtering method is used.

[0088] Moreover, the mask blank for EUVL 200 may further include, a protective film. The protective film is formed between the multi-layer reflective film 220 and the absorbing film 230. The protective film protects the multi-layer reflective film 220 in order for the multi-layer reflective film 220 not to be etched when the absorbing film 230 is etched to form the opening patterns 231 in the absorbing film 230. The protective film is formed from, for example, Ru, Si, TiO_2 , etc. As the protective film forming method, for example a sputtering method is used.

[0089] As shown in Fig. 12, a mask for EUVL 201 is obtained by forming the opening patterns 231 in the absorbing film 230 of the mask blank for EUVL 200. In order to form the opening patterns 231, a photolithography method and an etching method are used. Therefore, a resist film used to form the opening patterns 231 may be included in the mask blank

for EUVL 200.

[0090] Note that, the substrate 210 or the various functional films formed on the substrate 210 may be cleaned during the manufacturing processes of the mask blank for EUVL 200. Cleaning utilizing chemical reactions of acid or alkali, cleaning utilizing physical actions, cleaning combining the above, etc. is performed. Cleaning utilizing physical actions is ultrasonic cleaning, scrub, two-fluid cleaning, etc. Two-fluid cleaning is performed by mixing and injecting cleaning liquid and gas.

[0091] Ultrasonic cleaning is performed by, for example, a substrate cleaning apparatus 1 shown in Fig. 1. Ultrasonic cleaning is performed preferably at least one between the steps S104 and S105, the steps S105 and S106, the steps S106 and S107, and after the step S107. Moreover, although not shown, ultrasonic cleaning may be performed before and behind the low reflective film, a hard mask film, or the protective film.

EXAMPLES

[0092] Hereinafter, data of experiments are described. Example 1 below is a comparative example and examples 2-4 below are examples. Conditions of the experiments and results of evaluation of examples 1-4 are shown in Table 1.

[0093]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	
Cleaning Head	1	Pure Water	Pure Water	Pure Water	Pure Water	
	2	–	HF	SPM	SPM	
	3	–	Pure Water	Pure Water	Pure Water	
	4	–	–	HF	Alkaline Cleaner	
	5	–	–	Pure Water	Pure Water	
	6	–	–	SC1	–	
	7	–	–	Pure Water	–	
	Surface Density of Ce [10 ¹⁰ atoms/cm ²]		380	16	≤ 0.8	1.2
	Sum of Surface Densities of All the Elements Except for Si [%]		3.2	–	0.1	0.4
	Dummy Cleaning Time [hr]		30	3	16	–
Number of Particles Adhering to the Substrate		15.0	1.0	1.5	–	

[0094] In examples 1-4, after performing pretreatment of the cleaning head by supplying various cleaning liquids referred to in Table 1, in the order of the numbers referred to in Table 1, to the diaphragm of the cleaning head, dummy cleaning was performed, and then cleaning of the substrate was performed. The material of the diaphragm of the cleaning head was quartz glass. Cutting and

mechanical polishing were applied to the diaphragm in this order in advance. In mechanical polishing, the diaphragm was polished by cerium oxide particles.

[0095] In Table 1, "surface density of Ce" and "sum
5 of surface densities of all the elements except for Si" are measured by the TXRF method after the pretreatment of the cleaning head, before the dummy cleaning. As an X-ray source for the TXRF method, a W (tungsten) beam was used and surface density of
10 elements of atomic number 13-30 and 33-72 was measured. The most prevalent element was Si. "Sum of surface densities of all the elements except for Si" is the sum of surface densities of all elements except for Si, when the surface density of Si is regarded as
15 100%. A limit of detection (minimum limit of detection) of the measuring apparatus which measures surface density of each element by the TXRF method is 0.8×10^{10} atoms/cm².

[0096] Moreover, if the surface density of each of
20 the elements on the vibration surface of the cleaning head is measured by the TXRF method, the cleaning head is broken; therefore, a quartz glass plate was prepared besides the cleaning head. Cutting and mechanical polishing are applied to the quartz glass
25 plate in this order in advance, same as with the diaphragm of the cleaning head. In the mechanical polishing, the quartz glass plate is cleaned by cerium oxide particles. After supplying various cleaning liquids referred to in Table 1, in the order of the
30 numbers referred to in Table 1, to the quartz glass plate, the surface density of each element on the surface of the quartz glass plate is measured by the TXRF method.

[0097] In Table 1, "dummy cleaning time" means the time for the number of particles that adhere to the dummy substrate during the ultrasonic cleaning to stabilize to a certain amount. The number of particles that adhere to the dummy substrate during the ultrasonic cleaning is measured by calculating the difference in the numbers of the particles on the dummy substrate between before and after the ultrasonic cleaning.

[0098] In Table 1, "number of particles adhering the substrate" means the average of the number of the particles that adhere to the substrate by the ultrasonic cleaning after the dummy cleaning. The number of particles that adhere to the dummy substrate during the ultrasonic cleaning is measured by calculating the difference in the numbers of the particles on the dummy substrate between before and after the ultrasonic cleaning.

[0099] The number of the particles is measured by MAGICS Series of Lasertec Corporation. The number of the particles is a number of defects converted into 40 nm size of SiO₂ particles.

[0100] As shown in Table 1, in example 1, since neither the first chemical liquid (chemical liquid to dissolve cerium oxide) nor the second chemical liquid (chemical liquid to dissolve quartz glass) is supplied to the diaphragm of the cleaning head during the pretreatment of the cleaning head, "dummy cleaning time" is long and "number of particles on the substrate" is high. A surface of a quartz plate which has been pretreated same as the cleaning head has over 30×10^{10} atoms/cm² of "surface density of Ce", and has over 1.0% of "sum of surface densities

of all elements except for Si".

[0101] On the other hand, in example 2, since "HF" is supplied to the diaphragm of the cleaning head during the pretreatment, "dummy cleaning time" is short and "number of particles on the substrate" is low. "HF" corresponds to the second chemical liquid (chemical liquid to dissolve quartz glass). A surface of a quartz plate which has been pretreated same as the cleaning head has 30×10^{10} atoms/cm² or less of "surface density of Ce".

[0102] In example 3, since "SPM" and "HF" are supplied to the diaphragm of the cleaning head during the pretreatment in this order, "dummy cleaning time" is short and "number of particles on the substrate" is low. "SPM" corresponds to the first chemical liquid (chemical liquid to dissolve cerium oxide), and "HF" corresponds to the second chemical liquid (chemical liquid to dissolve quartz glass). A surface of a quartz plate which has been pretreated same as the cleaning head has 1×10^{10} atoms/cm² or less of "surface density of Ce", and has 1.0% or less of "surface density of all elements except Si".

[0103] In example 4, since "SPM" and "alkaline cleaner" are supplied to the diaphragm of the cleaning head during the pretreatment in this order, "dummy cleaning time" is short and "number of particles on the substrate" is low. "SPM" corresponds to the first chemical liquid (chemical liquid to dissolve cerium oxide), and "HF" corresponds to the second chemical liquid (chemical liquid to dissolve quartz glass). A surface of a quartz plate which has been pretreated same as the cleaning head has 10×10^{10} atoms/cm² or less of "surface density of Ce", and has 1.0% or less

of "surface density of all elements except Si".

[0104] Concerning embodiments above, the following additions are disclosed.

[ADDITION 1] An ultrasonic cleaning head including
5 a vibration surface that faces an upper surface of a substrate with a gap therebetween, and comes in contact with a liquid film formed on the upper surface of the substrate,

wherein the vibration surface has a surface
10 density of Ce element of 30×10^{10} atoms/cm² or less as detected by total reflection X-ray fluorescence analysis.

[ADDITION 2] The ultrasonic cleaning head according to addition 1, wherein the vibration surface has a
15 surface density of Ce element of 10×10^{10} atoms/cm² or less as detected by total reflection X-ray fluorescence analysis.

[ADDITION 3] The ultrasonic cleaning head according to addition 2, wherein the vibration surface has a
20 surface density of Ce element of 1×10^{10} atoms/cm² or less as detected by total reflection X-ray fluorescence analysis.

[ADDITION 4] The ultrasonic cleaning head according to any one of additions 1 to 3, wherein when surface
25 density of a most prevalent element among elements of atomic numbers 13-30 and 33-72 detected by total reflection X-ray fluorescence analysis is regarded as 100%, a sum of surface densities of all the elements except for the most prevalent element is 1.0% or less.

30 [ADDITION 5] The ultrasonic cleaning head according to addition 4, wherein the most prevalent element is Si.

[ADDITION 6] The ultrasonic cleaning head according

to addition 4, wherein a material of the vibration surface is SiO₂.

[ADDITION 7] A substrate cleaning method including:

limiting a surface density of Ce element
5 detected by total reflection X-ray fluorescence analysis to 30×10^{10} atoms/cm² or less, by supplying to a vibration surface of an ultrasonic cleaning head at least one of a first chemical liquid to dissolve cerium oxide and a second chemical liquid to dissolve
10 the vibration surface;

applying vibration from the vibration surface to a liquid film while forming the liquid film between the vibration surface of the ultrasonic cleaning head and an upper surface of a substrate facing each other,
15 after limiting the surface density of Ce element detected by the total reflection X-ray fluorescence analysis to 30×10^{10} atoms/cm² or less.

[ADDITION 8] A substrate cleaning apparatus including:

20 the ultrasonic cleaning head of any one of additions 1 to 3;

a retaining part configured to retain the substrate; and

a nozzle configured to form the liquid film on
25 the upper surface of the substrate retained with the retaining part.

[ADDITION 9] A substrate manufacturing method including cleaning a substrate using the substrate cleaning apparatus of addition 8.

30 [ADDITION 10] A method of manufacturing a mask blank for EUVL, including cleaning a glass substrate or a functional film formed on the glass substrate using the substrate cleaning apparatus of addition 8.

[0105] Although the ultrasonic cleaning head, the substrate cleaning methods, the substrate cleaning apparatuses, the substrate manufacturing methods, and the EUVL mask manufacturing methods are described above, the present invention is not limited to these embodiments. Various variations, modifications, replacements, additions, deletions, or combinations may be made without departing from the scope disclosed in the claims. They also obviously belong to the technical scope of the present disclosure.

[0106] The present application is based on and claims priority to Japanese patent application No. 2022-032933 filed on March 3, 2022 with the Japanese Patent Office, and the entire contents of Japanese patent application No. 2022-032933 are hereby incorporated by reference.

REFERENCE SIGNS LIST

20	[0107]	30	cleaning head (ultrasonic cleaning head)
		31a	vibration surface
		W	substrate
		Wa	upper surface of substrate
25		F	liquid film

Claims

[Claim 1] An ultrasonic cleaning head comprising a vibration surface that faces an upper surface of a substrate with a gap therebetween, and comes in
5 contact with a liquid film formed on the upper surface of the substrate,

wherein the vibration surface has a surface density of Ce element of 30×10^{10} atoms/cm² or less as detected by total reflection X-ray fluorescence
10 analysis.

[Claim 2] The ultrasonic cleaning head according to claim 1, wherein the vibration surface has a surface density of Ce element of 10×10^{10} atoms/cm² or less as detected by total reflection X-ray fluorescence
15 analysis.

[Claim 3] The ultrasonic cleaning head according to claim 2, wherein the vibration surface has a surface density of Ce element of 1×10^{10} atoms/cm² or less as detected by total reflection X-ray fluorescence
20 analysis.

[Claim 4] The ultrasonic cleaning head according to any one of claims 1 to 3, wherein when surface density of a most prevalent element among elements of atomic numbers 13-30 and 33-72 detected by total reflection
25 X-ray fluorescence analysis is regarded as 100%, a sum of surface densities of all the elements except for the most prevalent element is 1.0% or less.

[Claim 5] The ultrasonic cleaning head according to claim 4, wherein the most prevalent element is Si.

30 [Claim 6] The ultrasonic cleaning head according to claim 4, wherein a material of the vibration surface is SiO₂.

[Claim 7] A substrate cleaning method comprising:

limiting a surface density of Ce element detected by total reflection X-ray fluorescence analysis to 30×10^{10} atoms/cm² or less, by supplying to a vibration surface of an ultrasonic cleaning head
5 at least one of a first chemical liquid to dissolve cerium oxide and a second chemical liquid to dissolve the vibration surface;

applying vibration from the vibration surface to a liquid film while forming the liquid film between
10 the vibration surface of the ultrasonic cleaning head and an upper surface of a substrate facing each other, after limiting the surface density of Ce element detected by the total reflection X-ray fluorescence analysis to 30×10^{10} atoms/cm² or less.

15 [Claim 8] A substrate cleaning apparatus comprising:
the ultrasonic cleaning head of any one of claims 1 to 3;

a retaining part configured to retain the substrate; and

20 a nozzle configured to form the liquid film on the upper surface of the substrate retained with the retaining part.

[Claim 9] A substrate manufacturing method comprising cleaning a substrate using the substrate cleaning
25 apparatus of claim 8.

[Claim 10] A method of manufacturing a mask blank for EUVL, comprising cleaning a glass substrate or a functional film formed on the glass substrate using the substrate cleaning apparatus of claim 8.