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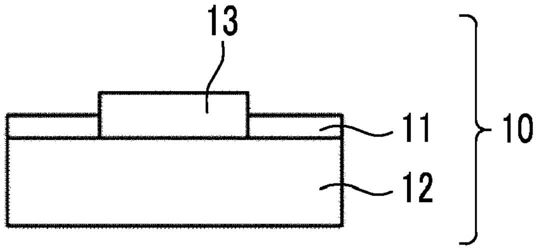
(54) ELECTROFORMING MASTER, METHOD FOR PRODUCING ELECTROFORMING MASTER, AND METHOD FOR PRODUCING ELECTROFORMING MATERIAL

(57) An electroforming master including an n-type semiconductor, and a substrate provided with a pattern on a surface thereof, in which an oxide film is formed on the surface, and a thickness of the oxide film is 18 Å or smaller, a method for producing the above-described electroforming master, and a method for producing an electroforming material using the above-described electroforming master.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present disclosure relates to an electroforming master, a method for producing an electroforming master, and a method for producing an electroforming material.

2. Description of the Related Art

[0002] An electroforming method is widely used as a method for producing parts having various shapes, dies, and the like. In the electroforming method, a master having a pattern on a surface thereof is used, and nickel or the like is electroformed on the master to produce an electroforming material.

[0003] For example, it is disclosed in JP2005-256110A to provide an electroforming mold including a plurality of mold structures consisting of silicon that is formed on a substrate consisting of silicon and that has side walls substantially perpendicular to a surface of the substrate, an insulator covering the side walls and an upper surface of each mold structure, and a support substrate that supports each mold structure through an insulating connection layer, in which the insulating connection layer connects a lower surface of each mold structure and an upper surface of the support substrate and includes a recessed portion that is formed such that at least a part of the insulating connection layer where each mold structure is not in contact is removed.

[0004] An oxide film is formed on a surface of the master over time, and the oxide film between an electroforming material during growth and the master exists to reduce the adhesive strength of the electroforming material to the master. As a result, there is a risk in which the electroforming material is peeled off on the way of production. Therefore, as described in JP2007-287216A, the oxide film is removed from the master using an acid such as hydrofluoric acid before the production of the electroforming material.

SUMMARY OF THE INVENTION

[0005] For the purpose of controlling a shape of an electroforming material, a pattern formed by an insulating film may be provided on a surface of a master.

[0006] The present inventor has found a knowledge that there is a difficulty in controlling the removal of an oxide film by using an acid, and a pattern may also be removed in a case where an oxide film is removed with respect to the master provided with the above-described pattern formed by the insulating film by using an acid.

[0007] In addition, the present inventor has also found that the adhesiveness of the electroforming material with respect to the electroforming master is improved by adjusting a thickness of the oxide film on a surface of a substrate provided in the electroforming master without removing the oxide film by an acid.

[0008] An object to be solved by an embodiment of the present disclosure is to provide an electroforming master that has excellent adhesiveness to an electroforming material and that is capable of suppressing an electroforming material during growth to be peeled off, a method for producing the above-described electroforming master, and a method for producing an electroforming material using the above-described electroforming master.

[0009] The specific means for solving the object is as follows.

<1> An electroforming master comprising an n-type semiconductor, and a substrate provided with a pattern on a surface thereof, in which an oxide film is formed on the surface, and a thickness of the oxide film is 18 Å or smaller.

<2> The electroforming master according to <1>, in which the oxide film contains a hydroxyl end-group.

<3> The electroforming master according to <1> or <2>, in which a contact angle of the oxide film with water at 23°C is 40° or smaller.

<4> The electroforming master according to any one of <1> to <3>, in which the n-type semiconductor is a silicon-based semiconductor.

<5> The electroforming master according to any one of <1> to <4>, in which the pattern is formed by an inorganic insulating film.

<6> The electroforming master according to <5>, in which the inorganic insulating film is a silicon-based oxide film.

<7> The electroforming master according to <5> or <6>, in which a thickness of the inorganic insulating film is 0.1 μm or greater.

<8> The electroforming master according to any one of <1> to <7>, in which a thickness of the oxide film is 2 Å or greater.

<9> A method for producing an electroforming master comprising a step of forming an oxide film having a thickness

of 18 Å or smaller by performing dry etching on a surface of a substrate that includes an n-type semiconductor and that is provided with a pattern on the surface, and exposing the substrate to an atmosphere.

<10> The method for producing an electroforming master according to <9>, in which a time of the exposure is 19 hours or shorter under conditions of 1 atm, 23°C ± 2°C, and a humidity of 50%RH ± 5%RH

<11> The method for producing an electroforming master according to <9> or <10>, in which the dry etching is performed using one or more gases selected from the group consisting of a rare gas, a fluorine-based gas, and a chlorine-based gas.

<12> The method for producing an electroforming master according to any one of <9> to <11>, in which the step of forming the oxide film includes performing one or more treatments selected from the group consisting of immersion in sulfuric acid-hydrogen peroxide, an UV ozone treatment, and an oxygen gas plasma treatment, on the substrate after the dry etching and before the exposure to the atmosphere.

<13> A method for producing an electroforming material comprising a step of forming, by using the electroforming master according to any one of <1> to <8> as a cathode, an electroforming material on the surface of the electroforming master on which the oxide film is formed, in an electroforming liquid, and

a step of peeling the electroforming material from the electroforming master.

<14> The method for producing an electroforming material according to <13>, further comprising a step of washing the electroforming master after the step of peeling the electroforming material from the electroforming master,

in which a cycle including the step of washing the electroforming master, the step of forming the electroforming material, and the step of peeling the electroforming material from the electroforming master is performed a plurality of times.

[0010] According to the present disclosure, it is possible to provide the electroforming master that has excellent adhesiveness to the electroforming material and that is capable of suppressing the electroforming material during growth to be peeled off, the method for producing the above-described electroforming master, and the method for producing an electroforming material using the above-described electroforming master.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

Fig. 1 is a schematic cross-sectional view illustrating an embodiment of an electroforming master of the present disclosure.

Fig. 2(A) to 2(E) is a schematic cross-sectional view illustrating an embodiment of a method for producing a substrate provided with a pattern on a surface thereof.

Fig. 3 is a schematic cross-sectional view illustrating an embodiment of an electroforming master and an electroforming material formed on a surface of the electroforming master.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] In the present disclosure, the numerical ranges expressed using "to" include the numerical values before and after the "to" as each of the minimum value and the maximum value.

[0013] In a range of numerical values described in stages in the present disclosure, the upper limit value or the lower limit value described in one range of numerical values may be replaced with an upper limit value or a lower limit value of the range of numerical values described in other stages. In addition, in a range of numerical values described in the present disclosure, the upper limit value or the lower limit value of the range of numerical values may be replaced with values illustrated in the examples.

[0014] In the present disclosure, an "n-type semiconductor" refers to a semiconductor in which free electrons are used as carriers that carry charges.

[0015] In the present disclosure, a "thickness of an oxide film" is measured as follows.

[0016] The thickness of the oxide film is measured at 23°C ± 2°C and 50%RH ± 5%RH in an atmosphere by using an ellipsometer. As the ellipsometer, an automatic ellipsometer DVA-36L manufactured by Mizojiri Optical Co., Ltd. or a similar device can be used.

[0017] A thickness of an inorganic insulating film or the like described later is also measured by the above-described method.

Electroforming Master

[0018] An electroforming master of the present disclosure includes an n-type semiconductor and a substrate provided with a pattern on a surface thereof, an oxide film is formed on the surface, and a thickness of the oxide film is 18 Å or smaller.

[0019] The electroforming master of the present disclosure has excellent adhesiveness to an electroforming material and can suppress the electroforming material during growth to be peeled off.

[0020] The reason why the above effect is achieved is presumed as follows, but is not limited thereto.

[0021] The thickness of the oxide film formed on the surface of the substrate included in the electroforming master of the present disclosure is 18 Å or smaller. It is presumed that since a decrease in electrostatic attraction between the substrate and the electroforming material to be grown on the oxide film is suppressed by setting the thickness of the oxide film to 18 Å or smaller, the electroforming master of the present disclosure has excellent adhesiveness to the electroforming material, and the electroforming material during growth is suppressed to be peeled off.

[0022] In addition, in a case where the oxide film is not formed on the surface of the electroforming master, it is difficult that the produced electroforming material is peeled off from the electroforming master, and there is a possibility that cohesion failure and the like may occur on the electroforming material or the electroforming master. It is presumed that the presence of the oxide film improves the adhesive strength between the electroforming material and the electroforming master, and enables the peeling while suppressing the occurrence of cohesion failure and the like.

[0023] A pattern provided on a surface of the substrate is not particularly limited, and it is preferable to appropriately adjust the pattern according to the application of the produced electroforming material. The method of forming the pattern will be described later.

[0024] From the viewpoint of improving the adhesiveness between the electroforming master and the electroforming material of the present disclosure, the thickness of the oxide film is preferably 17 Å or smaller, more preferably 15 Å or smaller, still more preferably 13 Å or smaller, and particularly preferably 10 Å or smaller.

[0025] The thickness of the oxide film is preferably 0.5 Å or greater, more preferably 1 Å or greater, still more preferably 2 Å or greater, and particularly preferably 5 Å or greater.

[0026] In a case where the oxide film is not formed on the surface of the electroforming master, it is difficult that the produced electroforming material is peeled off from the electroforming master, and there is a possibility that cohesion failure and the like may occur on the electroforming material or the electroforming master.

[0027] By setting the thickness of the oxide film to 0.5 Å or greater, the adhesive strength between the electroforming material and the electroforming master is improved, and the peeling can be achieved while suppressing the occurrence of cohesion failure and the like.

[0028] In addition, in a case of forming the electroforming material on the oxide film, it is possible to suppress inclusion of air bubbles between the oxide film and the electroforming material by setting the thickness of the oxide film to 0.5 Å or greater, and it is possible to suppress the occurrence of defects due to an increase in surface roughness of the electroforming material, which is caused by the air bubbles included.

[0029] The thickness of the oxide film can be adjusted by adjusting an exposure time of the substrate to the atmosphere after dry etching described later.

[0030] The oxide film preferably contains a hydroxyl end-group (-OH).

[0031] Since the oxide film contains the hydroxyl end-group (-OH), the hydrophilicity on the surface of the oxide film can be improved, it is possible to suppress the inclusion of the above-described air bubbles, and it is possible to suppress the occurrence of defects due to an increase in surface roughness of the electroforming material, which is caused by the air bubbles included.

[0032] Whether or not the oxide film contains a hydroxyl end-group is determined by X-ray photoelectron spectroscopy (XPS).

[0033] Specifically, whether or not a hydroxyl group derived from a silanol group is detected on the surface of the oxide film is confirmed under the following measurement conditions using an X-ray photoelectron spectroscope device.

[0034] In XPS, the X-ray source is monochromatic Al Kα ray, the X-ray spot diameter is 100 μm, and the photoelectron escape angle is 90° (inclination of a detector with respect to the surface of the oxide film).

[0035] The X-ray photoelectron spectroscope device is used for XPS, and for example, Axis-Ultra manufactured by Shimadzu Corporation or a similar device can be used.

[0036] A contact angle of the oxide film with water at 23°C is preferably 40° or smaller, more preferably 35° or smaller, still more preferably 30° or smaller, and particularly preferably 20°C or smaller.

[0037] By setting the contact angle of the oxide film with water at 23°C to 40° or smaller, it is possible to suppress the inclusion of the above-described air bubbles, and it is possible to suppress the occurrence of defects due to an increase in surface roughness of the electroforming material, which is caused by the air bubbles included.

[0038] In the present disclosure, the "contact angle of the oxide film with water at 23°C" is measured by a method of dropping water in air with a water droplet volume of 1 μL using a contact angle meter.

[0039] As the contact angle meter, for example, DMo-701 manufactured by Kyowa Interface Science Co., Ltd. or a similar device can be used.

[0040] The n-type semiconductor contained in the substrate is not particularly limited, and known n-type semiconductors in the related art can be used. Examples of the n-type semiconductor include silicon compounds (silicon-based semiconductors), fullerene compounds, electron-deficient phthalocyanine compounds, condensed ring polycyclic compounds (such as naphthalenetetracarbonyl compounds and perylenetetracarbonyl compounds), and tetracyanoquinodimethane compounds (such as TCNQ compounds), polythiophene compounds, benzidine compounds, carbazole compounds, phenanthroline compounds, and the like.

[0041] Among the above-described examples, the n-type semiconductor is preferably a silicon-based semiconductor from the viewpoint of improving the adhesiveness to the electroforming material. Examples of the silicon-based semiconductor include single crystal silicon, polycrystalline silicon, amorphous silicon, polysilicon, and the like.

[0042] From the viewpoint of improving the adhesiveness to the electroforming material, a thickness of the substrate is preferably 50 μm to 1,500 μm, more preferably 300 μm to 1,000 μm, and still more preferably 500 μm to 750 μm.

[0043] The pattern provided on the surface of the substrate is preferably formed by an inorganic insulating film.

[0044] Since the pattern provided on the surface of the substrate is formed by the inorganic insulating film, electroforming of nickel or the like on the pattern can be suppressed, and an electroforming material having a desired shape can be formed.

[0045] The inorganic insulating film for forming the pattern is preferably a silicon-based oxide film. For example, the inorganic insulating film can be an inorganic insulating film formed of silane dioxide.

[0046] Since the inorganic insulating film is a silicon-based oxide film, electroforming of nickel or the like on the pattern can be further suppressed, and an electroforming material having a desired formation can be produced. In addition, since the inorganic insulating film is a silicon-based oxide film, the adhesiveness to the substrate can be improved. Furthermore, according to the electroforming master including the substrate with the above pattern, in a case where the formed electroforming material is peeled off from the electroforming master, it is possible to suppress that the pattern is also peeled off, so that regeneration of the pattern is not required. Therefore, the electroforming master including the substrate with the above pattern is suitable for continuous production of the electroforming material and is preferable.

[0047] As the silicon-based oxide film, an oxide-containing film of the above-described silicon-based semiconductor can be used.

[0048] From the viewpoint of suppressing electroforming of nickel or the like, a thickness of the inorganic insulating film is preferably 0.1 μm or greater, more preferably 0.5 μm or greater, and still more preferably 1 μm or greater.

[0049] The upper limit of the thickness of the inorganic insulating film is not particularly limited, and may be, for example, 10 μm or smaller.

[0050] An embodiment of the electroforming master of the present disclosure will be described below with reference to Fig. 1.

[0051] An electroforming master 10 of the present disclosure includes a substrate 12 in which an oxide film 11 is formed on a surface thereof. The substrate 12 has a pattern 13 on the surface thereof.

[0052] The oxide film 11 is not formed on the surface of the pattern 13 in Fig. 1, but the oxide film 11 may be formed on a part or the entire surface of the pattern 13.

Method for producing Electroforming Master

[0053] A method for producing an electroforming master of the present disclosure includes a step of forming an oxide film having a thickness of 18 Å or smaller by performing dry etching on a surface of a substrate that includes an n-type semiconductor and that is provided with a pattern on the surface, and exposing the substrate to an atmosphere.

[0054] According to the method for producing an electroforming master of the present disclosure, it is possible to produce an electroforming master that has excellent adhesiveness to an electroforming material and can suppress the electroforming material during growth to be peeled off.

[0055] The reason why the above effect is achieved is presumed as follows, but is not limited thereto.

[0056] The electroforming master produced by the method for producing an electroforming master of the present disclosure includes the substrate, and the oxide film having a thickness of 18 Å or smaller is formed on the surface thereof. It is presumed that since a decrease in electrostatic attraction between the substrate and the electroforming material to be grown on the oxide film is suppressed by setting the thickness of the oxide film to 18 Å or smaller, the above-described electroforming master has excellent adhesiveness to the electroforming material, and the electroforming material during growth is suppressed to be peeled off.

[0057] In addition, according to the electroforming master produced by the method for producing an electroforming master of the present disclosure, in a case of forming the electroforming material on the oxide film, it is possible to suppress inclusion of air bubbles between the oxide film and the electroforming material, and it is possible to suppress the occurrence of defects due to an increase in surface roughness of the electroforming material, which is caused by the air bubbles included.

[0058] The reason why the above effect is achieved is presumed as follows, but is not limited thereto.

[0059] According to the method for producing an electroforming master of the present disclosure, it is not necessary to use an acid such as hydrofluoric acid, and the electroforming master can be produced by performing dry etching on the substrate and exposing the substrate to the atmosphere. Therefore, the surface of the oxide film tends to have excellent hydrophilicity. In a case of forming the electroforming material on the oxide film, it is possible to suppress inclusion of air bubbles between the oxide film and the electroforming material by the oxide film having excellent hydrophilicity, and it is possible to suppress the occurrence of defects due to an increase in surface roughness of the electroforming material, which is caused by the air bubbles included.

[0060] A method of performing dry etching on the surface of the substrate is not particularly limited, and the dry etching can be performed by using known etching gases in the related art.

[0061] By performing the dry etching on the substrate, the oxide film that is formed on the surface of the substrate in advance can be removed, and by exposing the substrate to the atmosphere, an oxide film having a thickness of 18 Å or smaller can be formed on the surface of the substrate.

[0062] For dry etching, it is preferable to use one or more gases selected from the group consisting of a rare gas, a fluorine-based gas, and a chlorine-based gas. By using the above gases, it is possible to prevent the oxide film from remaining on the surface of the substrate.

[0063] As the rare gas, He gas, Ar gas, and the like can be used.

[0064] As the fluorine-based gas, SF_6 gas, CF_4 gas, CHF_3 gas, C_2F_6 gas, C_4F_8 gas, and the like can be used.

[0065] As the chlorine-based gas, Cl_2 gas, $CHCl_3$ gas, CH_2Cl_2 gas, CCl_4 gas, BCl_3 gas, and the like can be used.

[0066] Among the above-described examples, SF_6 gas or Ar gas is preferable from the viewpoint that the surface of the electroforming material can be a mirror surface.

[0067] From the viewpoint of improving the adhesiveness of the electroforming master to the electroforming material, an exposure time to the atmosphere is preferably 24 hours or shorter, more preferably 19 hours or shorter, still more preferably 5 hours or shorter, and particularly preferably 1 hour or shorter, and may be 10 minutes or shorter, under the conditions of 1 atm, 23°C ± 2°C and a humidity of 50%RH ± 5%RH

[0068] The lower limit of the exposure time to the atmosphere is not particularly limited, and may be, for example, one minute or longer.

[0069] The step of forming the oxide film may include performing one or more treatments selected from the group consisting of immersion in sulfuric acid-hydrogen peroxide, an ultraviolet (UV) ozone treatment, and an oxygen gas plasma treatment, on the substrate after the dry etching and before the exposure to the atmosphere.

[0070] By including the above treatments in the step of forming the oxide film, the hydrophilicity on the surface of the oxide film can be improved, and it is possible to suppress inclusion of air bubbles between the oxide film and the electroforming material in a case of producing the electroforming material by using the electroforming master produced by the production method of the present disclosure, and it is possible to suppress the occurrence of defects due to an increase in surface roughness of the electroforming material, which is caused by the air bubbles included.

[0071] As the substrate provided with a pattern on the surface of the electroforming master used for the production, a commercially available substrate may be used, or a substrate produced by a known method in the related art may be used.

[0072] Hereinafter, an embodiment of a method for producing a substrate provided with a pattern on a surface thereof will be described with reference to Fig. 2(A) to 2(E).

[0073] First, a substrate 20 containing a silicon-based semiconductor is prepared, and one surface of the substrate 20 is thermally oxidized to form an inorganic insulating film 21 as a silicon-based oxide film (Fig. 2(A)).

[0074] A resist is applied to the surface of the inorganic insulating film 21 to form a resist film 22 (Fig. 2(B)).

[0075] The resist is not particularly limited, and an ultraviolet curable resin or the like in the related art, which is used for photolithography, can be used.

[0076] The resist film 22 is exposed in a patterned manner (Fig. 2(C)).

[0077] As illustrated in Fig. 2(C), the exposure of the resist film 22 can be performed in a patterned manner by using a known patterning mask 23 in the related art.

[0078] After the exposure, a known developer in the related art is used to remove an exposed portion of the resist film by washing to form a resist mask 24 (Fig. 2(D)).

[0079] After the resist mask 24 is formed, the inorganic insulating film 21 formed in a portion where the resist mask 24 is not formed is removed by dry etching, and the resist mask 24 is then peeled off, thereby capable of obtaining a substrate 26 provided with a pattern 25 (Fig. 2(E)).

Method for Producing Electroforming Material

[0080] The method for producing an electroforming material of the present disclosure includes a step of forming, by using the electroforming master as a cathode, an electroforming material on the surface of the electroforming master on which the oxide film is formed, in an electroforming liquid, and a step of peeling the electroforming material from the electroforming master.

[0081] According to the method for producing an electroforming material of the present disclosure, it is possible to suppress the electroforming material during growth to be peeled off from the electroforming master.

[0082] The reason why the above effect is achieved is presumed as follows, but is not limited thereto.

[0083] The electroforming master used in the method for producing an electroforming material of the present disclosure includes the substrate, and the oxide film having a thickness of 18 Å or smaller is formed on the surface thereof. It is presumed that since a decrease in electrostatic attraction between the substrate and the electroforming material to be grown on the oxide film is suppressed by setting the thickness of the oxide film to 18 Å or smaller, the above-described electroforming master has excellent adhesiveness to the electroforming material, and the electroforming material during growth is suppressed to be peeled off.

Step of Forming Electroforming Material

[0084] The electroforming material can be formed in the electroforming liquid by using the above-described electroforming master as a cathode through energization.

[0085] The electroforming liquid to be used is not particularly limited, and for example, nickel sulfamic acid electroforming liquid can be used.

[0086] A material that can be used as an anode is not particularly limited, and for example, a nickel plate can be used.

[0087] The current density and energization time in the energization are not particularly limited, and it is preferable to appropriately adjust the current density and energization time according to a desired size of the electroforming material to be formed.

[0088] For example, the current density can be $5A/dm^2$ to $10A/dm^2$, and the energization time can be 10 minutes to 2 hours.

[0089] The electroforming material may be formed only on the surface of the oxide film, but an electroforming material 32 grown on a surface of an oxide film 31 may be formed to ride on a pattern 33 formed by an inorganic insulating film (so-called overgrowth), as illustrated in Fig. 3. In Fig. 3, the substrate is denoted by the reference numeral 34.

Step of Peeling Electroforming Material

[0090] A method for peeling the electroforming material from the electroforming master is not particularly limited, and a known method in the related art can be used.

Step of Washing Electroforming Master

[0091] A method for producing an electroforming material of the present disclosure can include a step of washing the electroforming master after the step of peeling the electroforming material from the electroforming master.

[0092] In the method for producing an electroforming material of the present disclosure, it is preferable to perform a cycle including the step of washing the electroforming master, the step of forming the electroforming material, and the step of peeling the electroforming material from the electroforming master a plurality of times.

[0093] A method for washing the electroforming master is not particularly limited, and the electroforming master can be washed by a known method in the related art, and for example, the electroforming master can be washed by using a washing solution containing Caro's acid. Examples of the washing solution containing Caro's acid include SH303 manufactured by KANTO KAGAKU.

Examples

[0094] Hereinafter, the above-described embodiment will be specifically described by way of Examples; however, the above-described embodiment is not intended to be limited to these Examples.

Example 1

[0095] A substrate (thickness of 725 μm) containing a silicon-based semiconductor was prepared, and one surface of the substrate was thermally oxidized to form an inorganic insulating film having a thickness of 2 μm. The inorganic insulating film was a silicon-based oxide film containing silane dioxide.

[0096] A resist (MICROPOSIT (registered trademark) S1818G, manufactured by ROHM AND HAAS ELECTRONIC MATERIALS K.K.) was applied to the surface of the inorganic insulating film by spin coating to form a resist film, and the resist film was exposed in a patterned manner. After the exposure, a developer was used to remove an exposed portion of the resist film by washing to form a resist mask on the inorganic insulating film.

[0097] After forming the resist mask, the inorganic insulating film formed on a portion of the substrate where the resist mask was not formed was removed by a dry etching method using a mixed gas of CHF_3 and CF_4.

[0098] Next, the resist mask was peeled off to prepare a substrate provided with a pattern formed by the inorganic insulating film.

[0099] Conditions for dry etching included a CHF_3 gas flow rate of 24×10^{-4} m^3/hr, a CF_4 gas flow rate of 6×10^{-4} m^3/hr, a pressure of 0.6 Pa, an inductively coupled plasma (ICP) of 200 W, a bias of 30 W, a lower cooling temperature of 50°C, and a processing time of 80 minutes.

[0100] The above-described substrate was left to stand in an environment of 23°C and a humidity of 50%RH for 168 hours.

[0101] After being left to stand, dry etching was performed on the surface of the substrate on which the pattern is formed by using SF_6 gas, and the oxide film having a thickness of 25 Å, which is formed on the surface of the substrate on which the pattern is formed was removed.

[0102] After removing the oxide film, the substrate was exposed to an atmosphere for 5 minutes to form an oxide film on the above-described surface thereof, and an electroforming master was obtained.

[0103] Conditions for dry etching included a SF_6 gas flow rate of 6×10^{-4} m^3/hr, a pressure of 0.6 Pa, an inductively coupled plasma (ICP) of 500 W, a bias of 15 W, and a processing time of one minute.

[0104] Conditions of the exposed atmosphere included 1 atm, 23°C, a humidity of 50%RH, and an exposure time of 5 minutes.

[0105] A thickness of the oxide film formed on the surface of the electroforming master was 8 Å in the atmosphere at 23°C and 50%RH, which was measured with an ellipsometer (automatic ellipsometer DVA-36L manufactured by Mizojiri Optical Co., Ltd.).

Examples 2 to 5

[0106] Electroforming masters were produced in the same manner as in Example 1, except that the exposure time to the atmosphere was changed to times illustrated in Table 1. Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Example 6

[0107] An electroforming master was produced in the same manner as in Example 1, except that dry etching was performed with SF_6 gas and CHF_3 gas on a surface of a substrate on which a pattern was formed.

[0108] Conditions for dry etching included a SF_6 gas flow rate of 6×10^{-4} m^3/hr, a CHF_3 gas flow rate of 24×10^{-4} m^3/hr, a pressure of 0.6 Pa, an inductively coupled plasma of 500W, and a bias of 15W.

[0109] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Example 7

[0110] An electroforming master was produced in the same manner as in Example 1, except that dry etching was performed with Ar gas on a surface of a substrate on which a pattern was formed.

[0111] Conditions for dry etching included an Ar gas flow rate of 6×10^{-3} m^3/hr, a pressure of 3 Pa, an inductively coupled plasma of 300 W, a bias of 120 W, and a processing time of one minute.

[0112] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Example 8

[0113] An electroforming master was produced in the same manner as in Example 1, except that an oxygen gas plasma treatment was performed after dry etching using SF_6 gas was performed on a surface of a substrate on which a pattern is formed and before exposure to the atmosphere.

[0114] Conditions for oxygen gas plasma treatment included an O_2 gas flow rate of 18×10^{-3} m^3/hr, a pressure of 10 Pa, an inductively coupled plasma of 800 W, a bias of 100 W, and a processing time of one minute.

[0115] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Example 9

[0116] An electroforming master was produced in the same manner as in Example 1, except that immersion in sulfuric acid-hydrogen peroxide was performed after dry etching using SF_6 gas was performed on a surface of a substrate on which a pattern is formed and before exposure to the atmosphere.

[0117] The immersion in sulfuric acid-hydrogen peroxide was performed with SH303 manufactured by KANTO KAGAKU. under conditions of an immersion time of 20 minutes and a washing time of 5 minutes.

[0118] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Example 10

[0119] An electroforming master was produced in the same manner as in Example 1, except that an UV ozone treatment was performed after dry etching using SF_6 gas was performed on a surface of a substrate on which a pattern is formed and before exposure to the atmosphere.

[0120] The UV ozone treatment was performed by using an UV ozone washing device manufactured by SEN LIGHTS Co., Ltd. and irradiation with ultraviolet rays of a low-pressure mercury lamp (wavelength of 185 nm) for 5 minutes.

[0121] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Comparative Example 1

[0122] An electroforming master was obtained in the same manner as in Example 1, except that no dry etching using SF_6 gas was performed on a surface of a substrate on which a pattern is formed, and no exposure to the atmosphere was performed. Since no dry etching and no exposure to the atmosphere were performed, the surface treatment method and the exposure time to the atmosphere are described as "-" in Table 1.

[0123] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Comparative Example 2

[0124] An electroforming master was produced in the same manner as in Example 1, except that the exposure time to the atmosphere was changed for 116 hours illustrated in Table 1.

[0125] Thicknesses of oxide films were measured in the same manner as in Example 1, and the results are illustrated in Table 1.

Comparative Example 3

[0126] An electroforming master was obtained in the same manner as in Example 1, except that no exposure to the atmosphere was performed. Since no exposure to the atmosphere was performed, the exposure time to the atmosphere is described as "-" in Table 1.

[0127] Since it was confirmed that no oxide film was formed on the electroforming master of Comparative Example 3, the thickness of the oxide film is described as "-" in Table 1.

Contact Angle with Water

[0128] A contact angle of the oxide film with water, included in the electroforming master produced in each of Examples and Comparative Examples, was measured and illustrated in Table 1.

[0129] The contact angle with water was measured by a method of dropping water in air using DMo-701 manufactured by Kyowa Interface Science Co., Ltd. in an environment of 23°C. The water droplet volume used for the measurement was 1 μL.

Identification on End-group

[0130] An end-group on the surface of the oxide film included in the electroforming master produced in each of Examples and Comparative Examples was identified as follows.

[0131] First, the electroforming master was immersed in trifluoroacetic anhydride. Next, in a case where the end-groups on the surfaces of the oxide films were identified by detecting the presence of a trifluoromethyl group by XPS, all of the end-groups on the surfaces of the oxide films included in the electroforming masters produced in Examples and Comparative Examples were hydroxyl groups.

[0132] In XPS, the X-ray source is monochromatic Al Kα ray, the X-ray spot diameter is 100 μm, and the photoelectron escape angle is 90° (inclination of a detector with respect to the surface of the oxide film).

[0133] The X-ray photoelectron spectroscope device (Axis-Ultra manufactured by Shimadzu Corporation) was used as XPS.

[0134] Since it was confirmed that no oxide film was formed on the electroforming master of Comparative Example 3, the end-group is described as "-" in Table 1.

Evaluation of Adhesiveness between Electroforming Master and Electroforming Material

[0135] The electroforming master produced in each of Examples and Comparative Examples was used as a cathode and immersed in a nickel electroforming liquid, and energization was performed at a current density of 6.2 A/dm^2 for 50 minutes to electroform nickel on the surface of the electroforming master on which the oxide film was formed, thereby producing an electroforming material having a thickness of 50 μm. A nickel plate was used as an anode.

[0136] The current density was changed to 6.2 A/dm^2, and the energization time was changed to 10 minutes, thereby producing an electroforming material having a thickness of 10 μm in the same manner as described above.

[0137] The produced electroforming material was visually observed and evaluated based on the following evaluation standard. The evaluation results are illustrated in Table 1.

[0138] In Comparative Example 3, although no peeling of either the electroforming material having a thickness of 50 μm or the electroforming material having a thickness of 10 μm from the electroforming master was confirmed, cohesion failure of the electroforming material or the electroforming master occurred in a case where these electroforming materials were peeled off from the electroforming masters.

Evaluation Standard

[0139]

A: No peeling from electroforming master was confirmed in either electroforming material having thickness of 50 μm or electroforming material having thickness of 10 μm.

B: No peeling from electroforming master was confirmed in electroforming material having thickness of 10 μm, but peeling from electroforming master was confirmed in electroforming material having thickness of 50 μm.

C: Peeling from electroforming master was confirmed in both electroforming material having thickness of 50 μm and electroforming material having thickness of 10 μm.

Surface Roughness Ra

[0140] Regarding an evaluation of adhesiveness between the electroforming master and the electroforming material, the produced electroforming material was peeled off from the electroforming master, and a surface roughness Ra of a peeled surface of the electroforming material was measured by using a non-contact 3D surface roughness/shape measuring machine (New View 7300 manufactured by Zygo Corporation), and the measurement results are illustrated in Table 1.

[0141] In Comparative Example 1 and Comparative Example 2 in which peeling of the electroforming material from the electroforming master was confirmed during the production of the electroforming material, since the surface roughness Ra of the electroformed material was not measured, and the measurement results are described as "-" in Table 1.

[0142] The surface roughness Ra of the electroforming material having a thickness of 50 μm was measured in each of Examples and Comparative Examples evaluated as A in the adhesiveness evaluation, and the surface roughness Ra of the electroforming material having a thickness of 10 μm was measured in each of Examples and Comparative Examples evaluated as B in the adhesiveness evaluation.

Table 1

	Surface treatment method for surface of substrate on which pattern is formed	Exposure time to atmosphere	Thickness of oxide film [Å]	Contact angle with water [°]	End-group	Evaluation of adhesiveness	Surface roughness Ra [nm]
Example 1	Etching with SF_6 gas	5 minutes	8	28	-OH	A	3.0

(continued)

	Surface treatment method for surface of substrate on which pattern is formed	Exposure time to atmosphere	Thickness of oxide film [Å]	Contact angle with water [°]	End-group	Evaluation of adhesiveness	Surface roughness Ra [nm]
Example 2	Etching with SF_6 gas	One hour	15	29	-OH	A	3.3
Example 3	Etching with SF_6 gas	2.5 hours	16	31	-OH	A	8.6
Example 4	Etching with SF_6 gas	4.5 hours	17	31	-OH	A	8.7
Example 5	Etching with SF_6 gas	20 hours	18	27	-OH	B	8.7
Example 6	Etching with SF_6 gas and etching with CHF_3 gas	5 minutes	9	26	-OH	A	5.0
Example 7	Etching with Ar gas	5 minutes	7	11	-OH	A	2.1
Example 8	Etching with SF_6 gas and oxygen gas plasma treatment	5 minutes	14	24	-OH	A	9.0
Example 9	Etching with SF_6 gas and immersion in sulfuric acid-hydrogen peroxide	5 minutes	10	5	-OH	A	1.1
Example 10	Etching with SF_6 gas and UV ozone treatment	5 minutes	12	13	-OH	A	1.8
Comparative Example 1	-	-	20	19	-OH	C	-
Comparative Example 2	Etching with SF_6 gas	116 hours	22	30	-OH	C	-
Comparative Example 3	Etching with SF_6 gas	-	-	50	-	A	20.5

[0143] As is clear from the results illustrated in Table 1, it can be seen that the electroforming master including the oxide film having a thickness of 18 Å or smaller in each of Examples has excellent adhesive strength to the electroforming material, and peeling of the electroforming material during growth can be effectively suppressed.

[0144] It can be seen that the electroforming master including the oxide film having a thickness of 18 Å or greater in each of Comparative Examples had a lower adhesive strength to the electroforming master than the electroforming master in each of Examples, and the electroforming material during growth was peeled off.

Evaluation of Suitability for Repeated Use

[0145] Here, the suitability for repeated use of the electroforming master in each of Examples was evaluated by the following method.

[0146] First, the electroforming material produced for the evaluation of the adhesiveness between the electroforming master and the electroforming material was peeled off from the electroforming master in each of Examples 1 to 10, and the electroforming master was washed with SH303 manufactured by KANTO KAGAKU.

[0147] After washing, nickel was electroformed on the electroforming master by the above-described method to produce an electroforming material.

[0148] The production of the electroforming material, the peeling of the electroforming material, and the washing of the electroforming master were set as one cycle, and this cycle was repeated 5 times.

[0149] After the electroforming material was peeled off, a pattern on the surface of the substrate included in the electroforming master in each of Examples was visually observed, and it was confirmed that no pattern was peeled off, and it was confirmed that repeated use can be achieved.

[0150] In addition, as a result of performing the evaluation of the adhesiveness between the electroforming master and the electroforming material on the electroforming material produced in each cycle, it was confirmed that the evaluation results in Examples were the same as each other, and the adhesiveness to the electroforming material was not deteriorated even using multiple times.

Explanation of References

[0151]

10: Electroforming master
11: Oxide film
12: Substrate
13: Pattern
20: Substrate
21: Inorganic insulating film
22: Resist film
23: Patterning mask
24: Resist mask
25: Pattern
26: Substrate with pattern
31: Oxide film
32: Electroforming material
33: Pattern
34: substrate

Claims

1. An electroforming master comprising

   a substrate that includes an n-type semiconductor and that is provided with a pattern on a surface thereof,
   wherein an oxide film is formed on the surface, and
   a thickness of the oxide film is 18 Å or smaller.

2. The electroforming master according to claim 1,
   wherein the oxide film contains a hydroxyl end-group.

3. The electroforming master according to claim 1 or 2,
   wherein a contact angle of the oxide film with water at 23°C is 40° or smaller.

4. The electroforming master according to any one of claims 1 to 3,
   wherein the n-type semiconductor is a silicon-based semiconductor.

5. The electroforming master according to any one of claims 1 to 4,

wherein the pattern is formed by an inorganic insulating film.

6. The electroforming master according to claim 5,
wherein the inorganic insulating film is a silicon-based oxide film.

7. The electroforming master according to claim 5 or 6,
wherein a thickness of the inorganic insulating film is 0.1 μm or greater.

8. The electroforming master according to any one of claims 1 to 7,
wherein the thickness of the oxide film is 2 Å or greater.

9. A method for producing an electroforming master comprising
a step of forming an oxide film having a thickness of 18 Å or smaller by performing dry etching on a surface of a substrate that includes an n-type semiconductor and that is provided with a pattern on the surface, and exposing the substrate to an atmosphere.

10. The method for producing an electroforming master according to claim 9,
wherein a time of the exposure is 19 hours or shorter under conditions of 1 atm, 23°C ± 2°C, and a humidity of 50%RH ± 5%RH

11. The method for producing an electroforming master according to claim 9 or 10,
wherein the dry etching is performed using one or more gases selected from the group consisting of a rare gas, a fluorine-based gas, and a chlorine-based gas.

12. The method for producing an electroforming master according to any one of claims 9 to 11,
wherein the step of forming the oxide includes performing one or more treatments selected from the group consisting of immersion in sulfuric acid-hydrogen peroxide, an UV ozone treatment, and an oxygen gas plasma treatment, on the substrate after the dry etching and before the exposure to the atmosphere.

13. A method for producing an electroforming material comprising:

a step of forming, by using the electroforming master according to any one of claims 1 to 8 as a cathode, an electroforming material on the surface of the electroforming master on which the oxide film is formed, in an electroforming liquid; and
a step of peeling the electroforming material from the electroforming master.

14. The method for producing an electroforming material according to claim 13, further comprising

a step of washing the electroforming master after the step of peeling the electroforming material from the electroforming master,
wherein a cycle including the step of washing the electroforming master, the step of forming the electroforming material, and the step of peeling the electroforming material from the electroforming master is performed a plurality of times.

FIG. 1

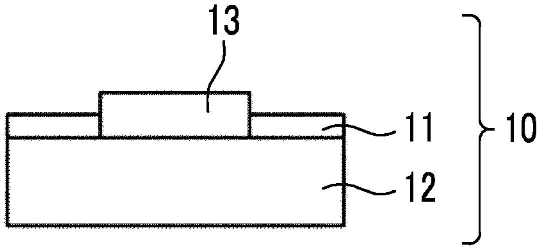


FIG. 2

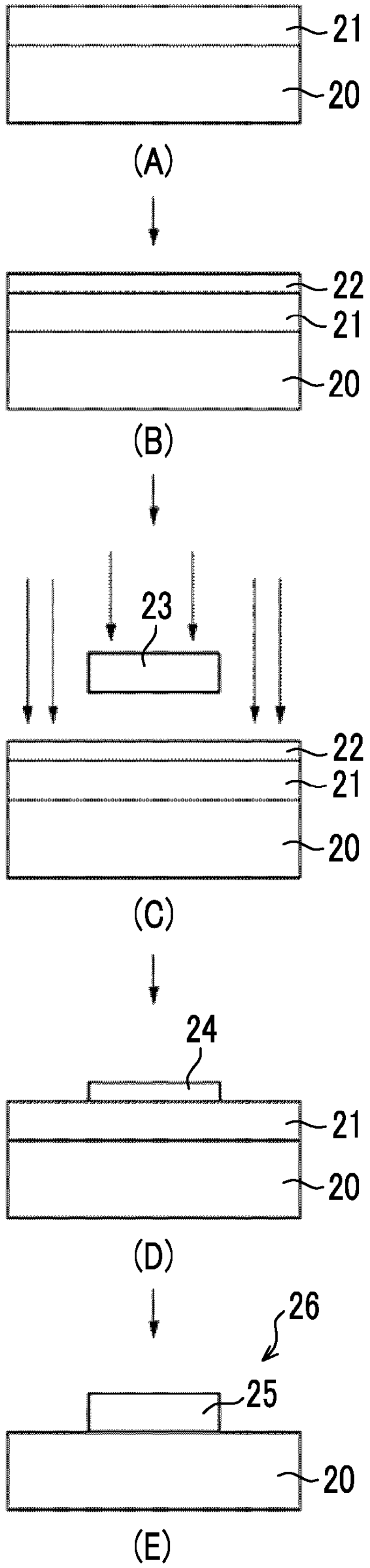
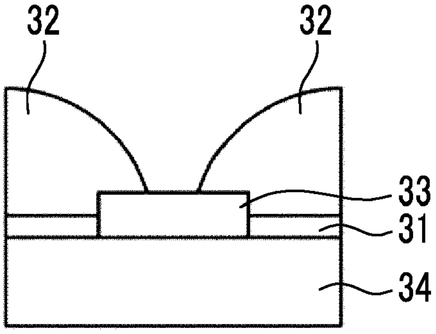


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	25 December 2022	Telias, Gabriela

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