

QUARTZ GLASS AND QUARTZ GLASS JIG HAVING EXCELLENT
RESISTANCE AGAINST PLASMA CORROSION,
AND METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

5 [0001]

1. Field of the Invention

The present invention relates to a quartz glass and a quartz jig for use in producing semiconductors yet having excellent resistance against plasma corrosion, and to a production method thereof.

10 [0002]

2. Description of the Related Art

In the production of semiconductors, for instance, in the production of semiconductor wafers, with the recent trend in increasing the diameter, the process efficiency is improved by using a plasma reaction apparatus in the etching process and the like. For instance, in
15 the process of etching semiconductor wafers, etching treatment is performed by using gaseous plasma; for example, a fluorine (F) based gaseous plasma.

[0003]

20 However, if a conventionally used quartz glass is placed, for instance, in a F-based gaseous plasma, SiO_2 undergoes reaction with the F-based gaseous plasma on the surface of the quartz glass surface as to generate SiF_4 . Since the boiling point of the thus generated SiF_4 is -86°C , it easily volatilizes as to cause large corrosion on the surface of the
25 quartz glass. Thus, quartz glass was found to be unsuitable for use as

jigs under a F-based gaseous plasma because thinning and surface roughening proceed on the surface of the quartz glass.

[0004]

As described above, severe problems were found to generate on
5 the conventional quartz glass in manufacturing semiconductors
employing plasma reaction concerning the resistance against plasma
corrosion, particularly, in case of applying etching treatment using a
F-based gaseous plasma. In the light of such circumstances, there is
proposed to cover the surface of the quartz glass member with aluminum
10 or an aluminum compound to improve the resistance against plasma
corrosion of the quartz glass member (see JP-A-Hei9-957751,
JP-A-Hei9-95772, and JP-A-Hei10-139480 (the term "JP-A" as referred
herein signifies "an unexamined published Japanese patent
application")), or to incorporate aluminum in quartz glass to improve the
15 resistance against plasma corrosion (JP-A-Hei11-228172).

[0005]

OBJECT AND SUMMARY OF THE INVENTION

The present inventors have extensively made studies to further
increase the resistance against plasma corrosion of quartz glass, and
20 among them, an investigation on the resistance against plasma corrosion
has been made for a quartz glass prepared by heating and fusing, in
vacuum, a quartz glass powder having mixed therein 5 % by weight of
alumina powder. On investigating the resistance against plasma
corrosion of the thus produced quartz glass, it has been found that the
25 etching rate thereof was lowered by 40 to 50 % as compared with that of

a quartz glass member free from doping.

[0006]

However, fine bubbles have been observed to generate inside and on the surface portion of the quartz glass body. Particularly on the surface portion, it has been found that a great difference occurred between the corroded portion and the non-corroded portion as to increase surface roughness. Furthermore, fine crystalline portions were found to generate as to frequently cause the problem of peeling off on those portions. This resulted in the generation of fine dimples and in the increased generation of particles that adhere to the surface of the wafer, thereby leading to problems such as an increase in defective wafers. In addition to above, since such bubbles and indentations accelerate etching, even though the concentration of the metal dope is increased, the resistance against plasma corrosion has been found to result in a relatively poor improvement.

[0007]

The reason for above is that the boiling point of AlF_3 , which generates on the reaction with the F-based plasma gas, is 1290°C , a temperature far higher than that of SiF_4 . Hence, presumably, while a large amount of the SiF_4 portion is corroded, little evaporation occurs on the surface of the AlF_3 portion, and this leads to a great difference in the etched quantity. Furthermore, if doped aluminum is locally concentrated, there occurs a clear difference in energy state as compared with the neighboring SiO_2 portions, and this causes a loss in balance as to easily cause a transition of SiO_2 to a crystalline state having lower

energy.

[0008]

The crystalline portions can be visually observed as fine white foreign matters. Since the crystalline portions that are formed in the vicinity of the surface have a thermal expansion differing from that of quartz glass, they tend to be easily peeled off with the change in temperature. Furthermore, since the metallic elements that are locally concentrated have lower boiling points than that of SiO_2 , they convert into gaseous phase on heating and fusing SiO_2 as to generate bubbles. The bubbles that are present in the vicinity of the surface easily explode with a change in temperature. The facts described above all lead to a cause of generating particles. Furthermore, since plasma gas concentrates on the bubbles and the indented portions to easily increase the etching rate, the total amount of etching of the entire glass increases to shorten the usable life of the glass.

[0009]

The present invention has been completed based on the above findings, and an object of the present invention is to provide a quartz glass as a material for jigs to use in the plasma reaction during the manufacture of semiconductors, yet having excellent corrosion resistance against plasma, particularly, F-based gaseous plasma. Another object of the present invention is to provide a quartz glass jig, and a further object of the present invention is to provide methods for producing the above.

[0010]

In order to overcome the aforementioned objects, according to a

first aspect of a quartz glass of the present invention, there is provided a quartz glass having excellent resistance against plasma corrosion, containing: a metallic element; and bubbles and foreign matters at an amount expressed by projected area of less than 100 mm^2 per 100 cm^3 .

5 [0011]

As an embodiment for incorporating the metallic element above, as a matter of course, not only doping and/or surface coating is included, but also, so long as the metallic element is incorporated at a predetermined concentration, any mode of incorporation can be
10 employed.

[0012]

If the content of the bubbles and the foreign matters of quartz glass is set to an amount expressed by projected area of less than 100 mm^2 per 100 cm^3 , this level provides a quartz glass member for general
15 use, and no particles generate in the plasma etching step. However, if the content of the bubbles and the foreign matters is not less than the range above, a large quantity of particles generates in the plasma etching step.

[0013]

20 The metal element to be incorporated in the quartz glass is not limited to Al (aluminum) or aluminum compounds that are disclosed in the aforementioned proposals, but usable in F-based gaseous plasma etching are other metallic elements so long as the fluoride of the metallic element yields a boiling point higher than that of the fluoride of Si. For
25 instance, usable are elements such as Ti, Zr, and Y, and rare earth

elements having a high resistance against etching corrosion, such as Sm. However, in case of a metallic element not favorable in the semiconductor industry, it should be used under the condition that the element imparts an extremely high corrosion resistance against etching
5 of the quartz glass.

[0014]

In case of employing mixing the metal oxide with quartz glass powder as a means for doping, melting is performed in a heating furnace or by Verneuil method; however, if the doped metal oxide yields a melting
10 point of 2,500 °C or higher, it is difficult to sufficiently melt the powder of the metallic oxide so long as a production method of the present art is employed. In such a case, a powder aggregate or a crystalline bulk remains to yield visually observable minute white foreign matters. Accordingly, it is preferred to dope metal oxides having a melting point
15 lower than 2,500 °C. Furthermore, not only a single metallic element is employed, but also effective is to co-dope a plurality of metallic elements.

[0015]

The concentration of the metallic elements above is preferably in the range of from 0.1 to 20 % by weight, and more preferably, 1.0 to 15 %
20 by weight. As a result of the experiments performed by changing the concentration of the metallic elements, if the concentration of the metallic elements is less than 0.1 % by weight, no improvement is observed on the resistance against etching corrosion. On the other hand, if the concentration should exceed 20 % by weight, the amount of doping
25 becomes too large to find any means unfeasible to suppress the

generation of bubbles and foreign matters.

[0016]

A first aspect of a quartz jig having excellent resistance against plasma corrosion according to the present invention is produced from the first aspect of the quartz glass as described above, and it has a metallic element-containing layer with a thickness to a predetermined depth and containing 0.1 to 20 % by weight of said metallic element. Preferably, the metallic element-containing layer is provided at a thickness of at least 5 mm.

10 [0017]

In case of a quartz glass jig for general use, the depth of corrosion occurring in contact with gaseous plasma is about 1 to 2 mm, or about 5 mm in maximum under conditions of general use, and it is hence possible to maintain the original shape and characteristics as a quartz glass jig. Accordingly, the preferred condition for using the first aspect of the quartz glass having excellent resistance against plasma corrosion of the present invention as the first aspect of the quartz glass jig of the present invention is to set the thickness of the metallic element-containing layer containing the metallic elements above at a concentration in a range of from 0.1 to 20 % by weight to at least 5 mm so as improve the etching resistance thereof.

[0018]

In incorporating the metallic elements in the metal element-containing layer, the metallic element may be doped in the quartz glass jig, and/or surface coating may be employed to coat the

surface of the quartz glass jig.

[0019]

A first aspect of a method for producing the quartz glass having excellent resistance against plasma corrosion according to the present invention comprises employing Verneuil process, i.e., a method for producing an ingot by using an oxyhydrogen flame, in which a quartz glass ingot having excellent resistance against plasma corrosion is produced from quartz powder. According to the process, a powder of the metallic element or a compound thereof is mixed with quartz powder, and then, the heated and fused resulting powder mixture is dropped to obtain a quartz glass ingot while heating the surface of the quartz glass ingot to a temperature of 1800 °C or higher, and preferably, at a temperature not higher than 3000 °C.

[0020]

According to a second aspect of a method for producing the quartz glass having excellent resistance against plasma corrosion of the present invention, there is provided a method for producing a quartz glass ingot having excellent resistance against plasma corrosion from quartz powder by means of Verneuil method, comprising, while preparing a quartz glass ingot by dropping the heated and fused quartz glass powder, continuously dropping on the growing surface of said quartz glass ingot, a solution prepared by dissolving a metallic element or a compound thereof in pure water, an acidic solution, an alkaline solution, or an organic solvent.

[0021]

In case of doping the quartz glass with a metallic element or of a compound thereof in the form of powder, heating and fusing must be carried out while applying sufficient heat energy, in such a manner that the powder of the metallic element or the powder of the compound may
5 be decomposed to the atomic or molecular level and be uniformly diffused and mixed with the quartz powder.

[0022]

In view of above, the metallic element is preferably doped in the form of a gas or a liquid. In case it is mixed in the form of powder, the
10 powder is preferably as finely divided as possible; in particular, since a metallic element tends to remain and concentrate in the SiO_2 network in the form of an oxide, preferably, the melting point of the oxide is as low as possible.

[0023]

15 In general, concerning the most commonly employed method comprising fusing a mixture of a quartz powder and a powder of a metallic element to be doped in a heating furnace, there is a limit in the high temperature region. Thus, it is extremely difficult to carry out a treatment at temperatures of 2000 °C or higher.

20 [0024]

In case of employing Verneuil method as the production process, the thermal energy that is supplied to a powder can be set high and at uniform density. Thus, a quartz glass body having less bubbles or foreign matters can be implemented. So long as a metal oxide having a
25 melting point up to about 2500 °C is used, fusion and diffusion of the

metallic oxide can be realized by setting the surface temperature of the ingot being formed in the vicinity of the melting temperature or even higher.

[0025]

5 As the powder, there is used a quartz powder containing mixed therein the metallic powder, an oxide, a nitrate compound, a chloride, and other compounds. Concerning the mode of doping, it is extremely effective to use, in the place of a powder, a solution uniformly dissolved therein a metallic element disintegrated to the atomic or molecular level,
10 which is dropped in the form of a liquid onto the growing surface of the ingot being formed, or sprayed to the growing surface of the ingot in the form of a volatilized gas or by using a carrier gas. As such a solution, there can be used a solution obtained by dissolving the metallic powder in an acidic or an alkaline solution, a solution obtained by dissolving a
15 nitrate compound in pure water, a solution obtained by dissolving a chloride compound in ethanol, a solution of an organometallic compound, or a solution obtained by dissolving the organometallic compound in an organic solvent.

[0026]

20 In accordance with a third aspect of a method for producing the quartz glass having excellent resistance against plasma corrosion of the present invention, there is provided a method comprising allowing a previously prepared porous SiO_2 body to stand still in an atmosphere containing the metallic element at a density in a range of from 0.1 to 10
25 mol per 22.4 liter, and applying a heat treatment thereto.

[0027]

The third aspect of the method of the present invention, which comprises diffusing and doping a doping substance in the gaseous state inside the porous body, can be defined as a CVD process. In the third
5 embodiment according to the method of the present invention, the porous SiO_2 body is allowed to stand still and subjected to a heat treatment in an atmosphere containing the metallic element at a gas density of (0.1 to 10 mol)/22.4 liter. After the treatment is continued for a long time until the gas is sufficiently diffused in the porous body, the temperature is
10 lowered so that the metallic element may reside uniformly inside the porous body in the form of oxides without causing local concentration. Since an increase in gas density increases the concentration of the oxide residing in the porous body, it is more effective to set the heating temperature as low as possible while setting the pressure as high as
15 possible. The heating temperature is preferably set to a temperature not lower than the boiling point, the gasification point, or the decomposition point of the metallic element or of the compound thereof, and the pressure is preferably set in a range of from 1 to 10 atoms.

[0028]

20 In accordance with a fourth aspect of a method for producing the quartz glass having excellent resistance against plasma corrosion of the present invention, there is provided a method which comprises preparing a slurry by dissolving in pure water, an acidic solution, an alkaline solution, or an organic solvent, a mixture of a quartz glass powder
25 having a particle size distribution in a range of from 0.01 to 1,000 μm

and containing from 1 to 50 % by weight of particles with its size ranging from 0.01 to 5 μm , with a metallic element or a compound thereof soluble in pure water, an acidic solution, an alkaline solution, or an organic solvent; drying and solidifying said slurry; and heating and fusing the solidified slurry in vacuum. This method is generally defined as a slip casting method.

[0029]

In the method comprising dissolving a quartz powder in pure water, mixing it with an aqueous solution of a metallic element to prepare a slurry, and forming therefrom a transparent solid by drying and heating in vacuum, it is necessary, for the drying and solidification, that the quartz powder has a particle size distribution as such that the particles 5 μm or less in size account for 1 to 50 % by weight of the powder. The particles 5 μm or less in size can be obtained by finely dividing the same quartz powder, or by using fumed silica prepared by flame hydrolysis of silicon tetrachloride.

[0030]

As an aqueous solution of the metallic element, there can be used such obtained by dissolving a metallic powder in an acidic or an alkaline solution, such obtained by dissolving a nitrate compound in pure water, such obtained by dissolving a chloride compound in an organic solvent such as ethanol, an organometallic compound or such obtained by dissolving it in an organic solvent. Particularly preferred is to use a solution obtained by dissolving a nitrate compound in pure water, because the resulting quartz glass body contains less bubbles.

[0031]

The method for preparing a quartz glass jig having an improved resistance against plasma corrosion comprises coating the surface of a previously prepared quartz glass jig with a solution prepared by mixing
5 and dissolving in pure water, an acidic solution, an alkaline solution, or an organic solvent, a metallic element or a compound thereof soluble in pure water, an acidic solution, an alkaline solution, or an organic solvent; followed by heating and fusing the thus coated surface.

[0032]

10 In case particular notice is made on increasing the concentration of the metallic element on the surface of the quartz glass jig, it is effective to employ a method comprising coating the surface of the quartz glass jig with the solution containing the metallic element and then applying heating thereto for fusion. As the solution containing the
15 metallic element, there can be used such prepared by dissolving a nitrate compound of the metallic element in pure water, such obtained by dissolving a chloride compound of the metallic element in an organic solvent such as ethanol, an organometallic compound containing the metallic element or such obtained by dissolving it in an organic solvent.
20 The solution thus obtained is then supplied dropwise, applied by using a brush, or sprayed to the surface of the quartz glass jig. As the solution of the metallic element, particularly preferred is an organometallic compound containing the metallic element or a solution prepared by dissolving it in an organic solvent.

25 [0033]

Then, the metallic element is fused on the surface and baked by means of flame melting, electric heating, arc melting, etc. In such a case, preferred is to use a quartz glass jig previously doped with a metallic element, because the metallic element can be incorporated at a high concentration in the entire body. Furthermore, such a quartz glass jig exhibits affinity with the surface containing the metallic element at a high concentration to prevent cracks and the like from being formed during cooling.

[0034]

As a previously prepared quartz glass jig, there can be used a known quartz glass jig, but favorably used is a quartz glass jig produced in accordance with the methods of the present invention for producing a quartz glass having excellent resistance against plasma corrosion described hereinbefore.

[0035]

As a means for measuring the local concentration of the metallic elements, usable is EPMA (Electron Probe Micro Analysis) to measure the planar distribution. Since the other portions are crystalline, X-ray diffraction or polarized optical microscope can be used for the detection.

[0036]

According to a second aspect of the present invention, there is provided a quartz glass having excellent resistance against plasma corrosion, characterized in that the corrosion resistance against plasma thereof is increased by adding a metallic element, said quartz glass containing bubbles and foreign matters at an amount as expressed by

projected area per 100 cm³ of less than 100 mm², having an OH concentration of 100 to 2000 ppm, having a surface roughness Ra of 0.01 to 10 μm, and a gas evolution of 2 mol/m³ or less in a temperature range of from room temperature to 1000 °C.

5 [0037]

As the metallic elements above, there can be used one type or two or more types of elements selected from the group consisting of Sm, Eu, Yb, Pm, Pr, Nd, Ce, Tb, Gd, Ba, Mg, Y, Tm, Dy, Ho, Er, Cd, Co, Cr, Cs, Zr, Al, In, Cu, Fe, Bi, Ga, and Ti.

10 [0038]

Since the metallic elements above each provide a fluoride having a boiling point high than that of Si, etching does not proceed as in the case of Si. The metallic elements are listed in the descending order of boiling point or gasification temperature; for instance, the boiling point of SmF is 2427 °C, and gasification temperature of TiF is 284 °C.

[0039]

The boiling point or the gasification temperature of the fluorides of metallic elements other than those enumerated above are too low to cause further etching. The concentration of the metallic elements above is preferably in the range of from 0.1 to 20 wt.%. If the metallic element should be incorporated at a concentration of less than 0.1 wt.%, no improvement on the resistance against etching would be expected; if the metallic element should be incorporated at a concentration exceeding 20 wt.%, bubbles or foreign matters would be generated in large quantities to make the glass unfeasible for use as jigs.

[0040]

Preferably, the quartz glass above has an internal transmittance for a visible radiation of 50 %/cm or higher.

[0041]

5 A second aspect of the quartz glass jig having excellent resistance against plasma corrosion according to the present invention is produced from the quartz glass of the present invention described above, and is characterized by being provided with a layer containing the metallic element in the range of from 0.1 to 20 % by weight with a thickness from
10 the surface to a predetermined depth. Preferably, the thickness of the layer containing the metallic element is at least 5 mm.

[0042]

In case of a commonly used quartz glass jig, the corrosion that occurs in contact with gaseous plasma is within a depth of about 1 to 2
15 mm, 5 mm in maximum, under the generally employed conditions. Hence, since the quartz glass jig can maintain the original shape and the characteristics in case of using the quartz glass having excellent resistance against plasma corrosion according to the present invention as a quartz glass jig, it is preferred to have its etching resistance improved
20 by providing at least a 5 mm thick layer containing the metallic elements above at a concentration of from 0.1 to 20 wt.%.

[0043]

In the second aspect of the quartz glass jig of the present invention, in respect of fashions of incorporating the metallic elements in
25 the layer containing the metallic element, they may be doped in the

quartz glass jig, and/or applied to the surface, followed by heating for diffusion.

[0044]

5 In the second aspect of the quartz glass jig according to the present invention, it is preferred that at least the surface to be brought into contact with the plasma corrosive gas is previously subjected to precision cutting, heating and fusing treatment, or heating and fusing treatment followed by chemical etching treatment.

[0045] -

10 In producing the second aspect of the quartz glass having excellent resistance against plasma corrosion according to the present invention, the following four methods can be employed. A first production method comprises employing Verneuil process, i.e., a method for producing an ingot by using an oxyhydrogen flame, in which a quartz
15 glass ingot having excellent resistance against plasma corrosion is produced from quartz powder. According to the method, a powder of the metallic element or a compound thereof is mixed with quartz powder, and then, the heated and fused resulting powder mixture is dropped to obtain a quartz glass ingot while heating the surface of the quartz glass
20 ingot to a temperature of 1800 °C or higher, and preferably, at a temperature not higher than 3000 °C.

[0046]

A second production method comprises producing a quartz glass ingot having excellent resistance against plasma corrosion from quartz
25 powder by means of Verneuil method; while preparing a quartz glass

ingot by dropping the heated and fused quartz glass powder, a solution prepared by dissolving a metallic element or a compound thereof in pure water, an acidic solution, an alkaline solution, or an organic solvent is continuously dropped on the growing surface of said quartz glass ingot.

5 [0047]

In case of doping the quartz glass with a metallic element or of a compound thereof in the form of powder, heating and fusing must be carried out while applying sufficient heat energy, in such a manner that the powder of the metallic element or the powder of the compound may
10 be decomposed to the atomic or molecular level and be uniformly diffused and mixed with the SiO_2 powder.

[0048]

In view of above, the metallic element is preferably doped in the form of a gas or a liquid. In case it is mixed in the form of powder, the
15 powder is preferably as finely divided as possible; in particular, since a metallic element tends to remain and concentrate in the SiO_2 network in the form of an oxide, preferably, the melting point of the oxide is as low as possible.

[0049]

20 Concerning the most commonly employed method comprising fusing a mixture of a quartz powder and a powder of a metallic element to be doped in a heating furnace, in general, there is a limit in the feasible high temperature region. Thus, it is extremely difficult to carry out a treatment at temperatures of 2000 °C or higher.

25 [0050]

In case of employing Verneuil method as the production process, the thermal energy that is supplied to a powder can be set high and at uniform density. Thus, a quartz glass body having less bubbles or foreign matters can be implemented. So long as a metal oxide having a
5 melting point up to about 2500 °C is used, fusion and diffusion of the metallic oxide can be realized by setting the surface temperature of the ingot formed in the vicinity of the melting temperature or even higher.

[0051]

As the powder, there is used a quartz powder containing mixed
10 therein the metallic powder, an oxide, a nitrate compound, a chloride, and other compounds. The mode of doping is extremely effective in which, in the place of a powder, a solution uniformly dissolved therein a metallic element disintegrated to the atomic or molecular level, which is dropped in the form of a liquid onto the growing surface of the ingot
15 being formed, or sprayed to the growing surface of the ingot in the form of a volatilized gas or by using a carrier gas. As such a solution, there can be used a solution obtained by dissolving the metallic powder in an acidic or an alkaline solution, a solution obtained by dissolving a nitrate compound in pure water, a solution obtained by dissolving a chlorine
20 compound in ethanol, a solution of an organometallic compound, or a solution obtained by dissolving a solid organometallic compound in an organic solvent.

[0052]

A third production method comprises allowing a previously
25 prepared porous SiO₂ body to stand still in an atmosphere containing the

metallic element at a density in a range of from 0.1 to 10 mol per 22.4 liter, and applying a heat treatment thereto.

[0053]

The third production method above, which comprises diffusing
5 and doping a doping substance in the gaseous state inside the porous
body, can be defined as a CVD process. In the third production method,
the porous SiO₂ body is allowed to stand still and subjected to a heat
treatment in an atmosphere containing the metallic element at a gas
density of (0.1 to 10 mol)/22.4 liter. - After the treatment is continued for
10 a long time until the gas is sufficiently diffused in the porous body, the
temperature is lowered so that the metallic element may reside
uniformly inside the porous body in the form of oxides without causing
local concentration. Since an increase in gas density increases the
concentration of the oxide residing in the porous body, it is more effective
15 to set the heating temperature as low as possible while setting the
pressure as high as possible. The heating temperature is preferably set
to a temperature not lower than the boiling point, the gasification point,
or the decomposition point of the metallic element or of the compound
thereof, and the pressure is preferably set in a range of from 1 to 10 atm.

20 [0054]

A fourth production method comprises preparing a slurry by
dissolving in pure water, an acidic solution, an alkaline solution, or an
organic solvent, a mixture of a quartz glass powder having a particle size
distribution in a range of from 0.01 to 1,000 μm and containing from 1 to
25 50 wt.% of group of particles with its size ranging from 0.01 to 5 μm ,

with a metallic element or a compound thereof soluble in pure water, an acidic solution, an alkaline solution, or an organic solvent; drying and solidifying said slurry; and heating and fusing the solidified slurry in vacuum. This method is generally defined as a slip casting method.

5 [0055]

In the method comprising dissolving a quartz powder in pure water, mixing it with an aqueous solution of a metallic element to prepare a slurry, and forming therefrom a transparent solid by drying and heating in vacuum, it is necessary for the drying and the
10 solidification that the quartz powder has a particle size distribution as such that the particles 5 μm or less in size account for 1 to 100 wt.%, preferably, 1 to 50 wt.%, of the powder. This group of particles can be obtained by finely dividing the same quartz powder, or by using fumed silica prepared by flame hydrolysis of silicon tetrachloride.

15 [0056]

As an aqueous solution of the metallic element, there can be used such obtained by dissolving a metallic powder in an acidic or alkaline solution, such obtained by dissolving a nitrate compound in pure water, such obtained by dissolving a chloride compound in an organic solvent
20 such as ethanol, an organometallic compound or such obtained by dissolving it in an organic solvent. Particularly preferred is to use a solution obtained by dissolving a nitrate compound in pure water, because the resulting quartz glass body contains less bubbles.

[0057]

25 The method for preparing the second aspect of the quartz glass

jig having an improved resistance against plasma corrosion according to the present invention comprises coating the surface of a previously prepared quartz glass jig with a solution prepared by mixing and dissolving in pure water, an acidic solution, an alkaline solution, or an
5 organic solvent, a metallic element or a compound thereof soluble in pure water, an acidic solution, an alkaline solution, or an organic solvent; followed by heating and fusing the thus coated surface.

[0058]

Particularly, where the particular notice is made on increasing
10 the concentration of the metallic element on the surface of the quartz glass jig, it is effective to employ a method comprising coating the surface of the quartz glass jig with the solution containing the metallic element and then applying heating thereto for fusion. As the solution containing the metallic element, there can be used such obtained by
15 dissolving a metallic powder in an acidic or alkaline solution, such prepared by dissolving a nitrate compound of the metallic element in pure water, such obtained by dissolving a chloride compound of the metallic element in an organic solvent such as ethanol, an organometallic compound containing the metallic element or such
20 obtained by dissolving it in an organic solvent. The solution thus obtained is then supplied dropwise, applied by using a brush, or sprayed to the surface of the quartz glass jig. As the solution of the metallic element, particularly preferred is a nitrate compound containing the metallic element, or a solution prepared by dissolving it in pure water.

25 [0059]

Then, the metallic element is fused on the surface and baked by means of flame fusion, electric heating, arc melting, etc. In such a case, preferred is to use a quartz glass jig previously doped with a metallic element, because the metallic element can be incorporated at a high concentration in the entire body. Furthermore, such a quartz glass jig exhibits affinity with the surface containing the metallic element at a high concentration, and it prevents cracks and the like from being formed during cooling.

[0060]

As a previously prepared quartz glass jig, there can be used a known quartz glass jig, but favorably used is a quartz glass jig produced in accordance with the methods of the present invention for producing a quartz glass having excellent resistance against plasma corrosion described hereinbefore.

[0061]

As a means for measuring the local concentration of the metallic elements, usable is EPMA (Electron Probe Micro Analysis) to measure the planar distribution. Since the corresponding portions are crystalline, X-ray diffraction or polarized optical microscope can be used for the detection.

[0062]

As to the quartz glass of the prior art containing the metallic elements in a range of from 0.1 to 20 wt%, bubbles and foreign matters were frequently generated. According to the present invention however, the quartz glass having less bubbles and foreign matters generated and

of the excellent internal transmittance of the visible radiation of 50 %/cm or higher can be obtained.

[0063]

The second aspect of the quartz glass body according to the present invention is subjected to a precision cutting treatment, a heating and melting treatment, or a frost treatment (heating and melting treatment followed by a chemical etching treatment), so that the surface roughness thereof falls in a range of from 0.01 to 10 μm . By providing such a surface state, fine cracks on the surface can be removed after mechanical processing to suppress the generation of initial particles on applying plasma etching.

[0064]

The precision cutting treatment comprises precision cutting the surface of the glass body by using a machine, and is advantageous in that less surface cracks are generated. The heating and melting treatment comprises performing surface heating and thereby fusion removing the surface cracks by means of gas combustion using oxyhydrogen, acetylene, etc., or by utilizing an electric heating source such as arc power.

[0065]

The frost treatment comprises subjecting a surface of the glass body to a heating and melting treatment, followed by immersing the resulting surface into a mixed solution of HF , acetic acid, ammonium fluoride, and pure water (which may be substituted by a solution containing 10 to 50 wt.% HF), thereby removing the surface layer by

etching while simultaneously forming a uniform surface. The quartz glass bodies thus obtained by any of the processes above contains residual OH at a high concentration attributed to the production method.

[0066]

5 The OH concentration of the second aspect of the quartz glass according to the present invention is in a range of from 100 to 2,000 ppm. If the OH concentration should be 100 ppm or higher, the effect of holding the alkali metals passing and diffusing through the quartz glass body becomes higher to prevent external contamination from occurring
10 on the wafer. However, if the OH concentration should exceed 2,000 ppm, the viscosity becomes excessively low to disadvantageously cause undesirable deformation of the wafer.

[0067]

15 In the second aspect of the quartz glass of the present invention, the amount of gas evolved in a temperature range of from room temperature to 1000 °C is 2 mol/m³ or less. Since the quartz glass body obtained through the process above is produced in the high temperature region of 1000 °C or higher, the previously occluded gas that is discharged up to 1000 °C amounts to a total of 2 mol/m³ or less. Since
20 the etching process is carried out in the temperature range of several hundreds of degrees Celsius, the actual amount of evolved gas is less than the total. Such a trace quantity of evolved gas does not affect the quality of the wafer when brought into contact with the wafer, nor influences the gaseous plasma.

25 [0068]

EXAMPLES AND COMPARATIVE EXAMPLES

The present invention is described in further detail below by way of examples, but it should be understood that these are provided only for exemplification, and that are by no means limiting.

5 [0069]

(Example 1)

A 1900-g portion of quartz particles were mixed with 100 g of Al_2O_3 powder, and the resulting mixture was dropped and fused in an oxyhydrogen flame at a rate of 50 g/min on a target ingot being rotated
10 at a speed of 1 rpm to obtain a quartz glass ingot 200 mm in diameter and 50 mm in length. The gas condition was set to flow gaseous H_2 at a rate of 200 liter/min and gaseous O_2 at a rate of 100 liter/min. The target ingot was then set inside a vessel having a volume 300 mm $\times$ 300 mm $\times$ 200 mm in height. If the gases should be flown at a rate lower
15 than the conditions above, bubbles and foreign matters were observed to generate, and if they should be flown at a rate higher than above, the shape of the ingot was no longer retained. The temperature of the growing plane of the ingot was found to be 2,200 °C.

[0070]

20 The ingot thus prepared was subjected to fluorescent X-ray analysis to obtain aluminum concentration. As a result, the average concentration in a region from the surface ranging to a depth of 0.1 mm was found to be 3.0 % by weight, and the concentration at a position 5.0 mm in depth from the surface was found to be 2.0 % by weight.
25 Excluding the surface, the average concentration for the overall region of

the thus formed ingot was found to be approximately 2.0 % by weight. The outermost surface portion is believed to yield a high concentration due to progressive gasification of quartz.

[0071]

5 Then, the content of bubbles and foreign matters of thus formed ingot was measured, and the presence of foreign matters of thus formed ingot was detected by means of X-ray diffraction. The results are given in Table 1. No foreign matter was present, and the content of bubbles and foreign matters was found to be 39 mm².

10 [0072]

 Furthermore, as described hereinafter, the amount of particle generation and the etching rate were measured, and the results are given in Table 1. The amount of generated particles was found to be low, and the etching rate was sufficiently low. Thus, it has been confirmed
15 that the product has excellent resistance against plasma corrosion.

[0073]

(Example 2)

 Quartz particles were dropped and fused in an oxyhydrogen flame at a rate of 50 g/min on a target ingot being rotated at a speed of 1 rpm,
20 and simultaneously, a 30% aqueous solution of aluminum nitrate was supplied dropwise to the growing surface of the ingot at a rate of 10 cc/min to obtain a quartz glass ingot 200 mm in diameter and 50 mm in length. The gas condition was set to flow gaseous H₂ at a rate of 150 liter/min and gaseous O₂ at a rate of 75 liter/min. The target ingot was
25 then set inside a vessel having a volume 300 mm × 300 mm × 200 mm

high.

[0074]

On measuring the aluminum concentration of the thus prepared quartz glass ingot by means of fluorescent X-ray analysis, a
5 concentration of 3.0 wt.% was obtained for the outermost surface portion (to a depth of 0.1 mm from the surface) and 1.0 wt.% for the portion at a depth of 5 mm from the surface. The outermost surface portion is believed to yield a high concentration due to progressive gasification of quartz. The average concentration over the entire length of the thus
10 formed ingot was found to be approximately 1.5 wt.%. Furthermore, measurements were performed for items similar to those described in Example 1, and the thus obtained results are given in Table 1. From the results shown in Table 1, it has been confirmed that the product yields excellent resistance against plasma corrosion.

15 [0075]

(Example 3)

A quartz glass ingot was prepared in the same manner as in Example 2, except for using zirconium oxonitrate as a doping material in the place of aluminum nitrate. The zirconium concentration was
20 measured for the thus prepared quartz glass ingot, and measurements were performed for the items similar to those described in Example 1. The results are given in Table 1. It has been confirmed that the product yields excellent resistance against plasma corrosion.

[0076]

25 (Example 4)

A quartz glass ingot was prepared in the same manner as in Example 2, except for using yttrium nitrate as a doping material in the place of aluminum nitrate. The yttrium concentration was measured for the thus prepared quartz glass ingot, and measurements were performed for the items similar to those described in Example 1. The results are given in Table 1. It has been confirmed that the product yields excellent resistance against plasma corrosion.

[0077]

Table 1

Example No.		1	2	3	4
Production method		Verneuil	Verneuil	Verneuil	Verneuil
Metallic element compound		Al ₂ O ₃ 5 wt. %	Pure water + aluminum nitrate	Pure water + zirconium oxonitrate	Pure water + yttrium nitrate
State of sample before etching test	Bubbles (mm ²)	19	18	18	29
	Foreign matters (mm ²)	20	20	17	28
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt. %)		2.0	1.5	1.9	1.8
Particles generated (particles)		11	13	11	9
Etching rate (nm/min)		35	35	33	40

*1 XRD: X-ray diffraction

[0078]

(Example 5)

A quartz glass ingot was prepared in the same manner as in Example 2, except for using samarium nitrate as a doping material in the place of aluminum nitrate. The samarium concentration was measured for the thus prepared quartz glass ingot, and measurements were performed for the items similar to those described in Example 1. The results are given in Table 2. It has been confirmed from the results in Table 2 that the product yields excellent resistance against plasma

corrosion.

[0079]

(Example 6)

A quartz glass ingot was prepared in the same manner as in
5 Example 2, except for using a solution prepared by dissolving 30 wt.% of
aluminum chloride in ethanol for use as the doping material in the place
of the 30 wt.% aqueous solution of aluminum nitrate. The aluminum
concentration was measured for the thus prepared quartz glass ingot,
and measurements were performed for the items similar to those
10 described in Example 1. The results are given in Table 2. It has been
confirmed from the results in Table 2 that the product yields excellent
resistance against plasma corrosion.

[0080]

(Example 7)

15 A quartz glass ingot was prepared in the same manner as in
Example 2, except for using a solution prepared by dissolving 5 wt.% of
aluminum in hydrochloric acid for the doping material in the place of the
30 wt.% aqueous solution of aluminum nitrate. The aluminum
concentration was measured for the thus prepared quartz glass ingot,
20 and measurements were performed for the items similar to those
described in Example 1. The results are given in Table 2. It has been
confirmed from the results in Table 2 that the product yields excellent
resistance against plasma corrosion.

[0081]

25 (Example 8)

A quartz glass ingot was prepared in the same manner as in Example 2, except for using a solution prepared by dissolving 30 wt.% of Al isopropoxide in propanol for the doping material in the place of the 30 wt.% aqueous solution of aluminum nitrate. The aluminum concentration was measured for the thus prepared quartz glass ingot, and measurements were performed for the items similar to those described in Example 1. The results are given in Table 2. It has been confirmed from the results in Table 2 that the product yields excellent resistance against plasma corrosion.

10 [0082]

Table 2

Example No.		5	6	7	8
Production method		Verneuil	Verneuil	Verneuil	Verneuil
Metallic element compound		Pure water + samarium nitrate	Ethanol + AlCl ₃	Hydrochloric acid + aluminum	Propanol + Al iso-propoxide
State of sample before etching test	Bubbles (mm ²)	17	20	15	20
	Foreign matters (mm ²)	29	23	29	28
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt.%)		1.3	2.0	2.4	1.3
Particles generated (particles)		13	15	13	10
Etching rate (nm/min)		32	31	30	30

*1 XRD: X-ray diffraction

[0083]

(Example 9)

15 A quartz glass ingot was prepared in the same manner as in Example 2, except for using a solution prepared by dissolving 30 wt.% of aluminum isopropoxide in ethyl silicate for the doping material in the place of the 30 wt.% aqueous solution of aluminum nitrate. The aluminum concentration was measured for the thus prepared quartz

glass ingot, and measurements were performed for the items similar to those described in Example 1. The results are given in Table 3. It has been confirmed from the results in Table 3 that the product yields excellent resistance against plasma corrosion.

5 [0084]

(Example 10)

A silica glass preform 500 mm in diameter and 1,000 mm in height prepared by soot method was set inside a quartz glass vessel 600 mm in diameter and 1,200 mm in height together with 500 g of
10 aluminum chloride granules, and after replacing the atmosphere to gaseous N₂, the gas inlet line was stopped, and heating was initiated to elevate the temperature to 400 °C, thereby gasifying all of aluminum chloride to obtain an atmosphere containing 100 % aluminum chloride. The state was maintained for 10 hours under the atmospheric condition,
15 at which heating was stopped to lower the temperature to room temperature. The soot was taken out of the vessel, and was placed inside a vacuum furnace to elevate the temperature to 1,800 °C to obtain a transparent glass body.

[0085]

20 From the surface portion of the thus obtained quartz glass, 3 wt.% of aluminum was detected, but for a portion at a depth of 5 mm from the surface, the aluminum concentration was found to be 2.0 wt.%. Thus formed quartz glass was found to have an average aluminum concentration of ca. 1.1 wt.%. Aluminum was detected in high
25 concentration on the surface, presumably due to the residual alumina

while SiO_2 underwent gasification during the vitrification of the soot into a transparent body.

[0086]

The boiling point of aluminum chloride is 180°C , however, at a treatment temperature of 150°C or lower, the gasification vapor pressure decreases to 70 mmHg or lower. The concentration of gaseous aluminum chloride in the atmosphere was found to be 0.08 mol/22.4 liter, and that in the glass was found to be about 0.01 wt.%. Thus, at a temperature exceeding 633°C , the aluminum concentration in the atmosphere became 0.5 mol/22.4 liter, and that of the glass thus obtained was found to be halved.

[0087]

Measurements were made on the same items as those in Example 1, and the results are given in Table 3. It has been confirmed from the results in Table 3 that the product yields excellent resistance against plasma corrosion.

[0088]

(Example 11)

A silica glass preform 500 mm in diameter and 1,000 mm in length prepared by soot method was set inside an airtight high pressure vessel together with 500 g of aluminum chloride granules, and after replacing the atmosphere to gaseous N_2 , the gas inlet line was stopped, and heating was initiated to elevate the temperature to 250°C , thereby gasifying all of aluminum chloride to obtain a high pressure atmosphere of 10 kg/cm², i.e., an atmosphere having a concentration of 9 mol/22.4

liter. The state was maintained for 10 hours, at which heating was stopped to lower the temperature to room temperature and the soot was taken out of the vessel.

[0089]

5 The soot taken out of the vessel was placed inside a vacuum furnace to elevate the temperature to 1,800 °C to obtain a transparent glass body. From the surface portion of the thus obtained quartz glass, 6 wt.% of aluminum was detected, but for a portion at a depth of 5 mm from the surface, the aluminum concentration was found to be 3.0 wt.%.
10 Thus formed quartz glass was found to have an average aluminum concentration of ca. 4.0 wt.%. The gaseous aluminum chloride concentration of the atmosphere, the aluminum concentration of the glass, and the aluminum concentration of the resulting glass were about the same as those obtained in Example 10.

15 [0090]

Furthermore, measurements were performed for the same items as those in Example 1, and the results are given in Table 3. It has been confirmed from the results in Table 3 that the product yields excellent resistance against plasma corrosion.

20 [0091]

(Example 12)

A quartz glass ingot was prepared in the same manner as in Example 10, except for using zirconium chloride granules as the doping material in the place of aluminum chloride granules, and for gasifying
25 all of zirconium chloride by elevating the temperature to 500 °C. The

zirconium concentration of the thus obtained quartz glass ingot was measured, and measurements were performed for the same items as those in Example 1. The results are given in Table 3. It has been confirmed from the results in Table 3 that the product yields excellent resistance against plasma corrosion.

[0092]

Table 3

Example No.		9	10	11	12
Production method		Verneuil	CVD	CVD	CVD
Metallic element compound		Ethyl silicate + Al isopropoxide	AlCl ₃	AlCl ₃	ZrCl ₄
State of sample before etching test	Bubbles (mm ²)	18	20	18	31
	Foreign matters (mm ²)	12	40	23	24
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt.%)		1.2	1.1	4.0	1.8
Particles generated (particles)		10	16	8	15
Etching rate (nm/min)		40	44	22	34

*1 XRD: X-ray diffraction

[0093]

10 (Example 13)

Slurry was prepared by mixing 750 g of quartz powder consisting of particles 500 to 100 μ m in particle diameter, 200 g of pyrolytic silica particles 0.01 to 4 μ m in particle diameter, 700 g of aluminum nitrate, and 1,500 g of pure water. The slurry was dried for 8 days in air at 40 °C to obtain a solid, and the resulting solid was subjected to a heat treatment at 1,800 °C for 1 hour in vacuum to prepare transparent glass 100 mm in diameter and 50 mm in height. The aluminum concentration for the whole bulk was found to be 2.0 wt.%.

[0094]

Measurements were made on the same items as those in Example 1, and the results are given in Table 4. It has been confirmed from the results in Table 4 that the product yields excellent resistance against plasma corrosion.

5 [0095]

(Example 14)

Quartz glass ingot was prepared in the same manner as in Example 13, except for using zirconium oxonitrate as the doping material in the place of aluminum nitrate. Measurements were
10 performed on the resulting quartz glass ingot for the zirconium concentration and the same items as those measured in Example 1. The results are given in Table 4. It has been confirmed from the results in Table 4 that the product yields excellent resistance against plasma corrosion.

15 [0096]

(Example 15)

Quartz glass ingot was prepared in the same manner as in Example 13, except for using yttrium nitrate as the doping material in the place of aluminum nitrate. Measurements were performed on the
20 resulting quartz glass ingot for the yttrium concentration and the same items as those measured in Example 1. The results are given in Table 4. It has been confirmed from the results in Table 4 that the product yields excellent resistance against plasma corrosion.

[0097]

25 (Example 16)

Quartz glass ingot was prepared in the same manner as in Example 13, except for using samarium nitrate as the doping material in the place of aluminum nitrate. Measurements were performed on the resulting quartz glass ingot for the samarium concentration and the same items as those measured in Example 1. The results are given in Table 4. It has been confirmed from the results in Table 4 that the product yields excellent resistance against plasma corrosion.

[0098]

Table 4

Example No.		13	14	15	16
Production method		Slip	Slip	Slip	Slip
Metallic element compound		Pure water+ aluminum nitrate	Pure water + zirconium oxonitrate	Pure water + yttrium nitrate	Pure water + samarium nitrate
State of sample before etching test	Bubbles (mm ²)	18	25	24	19
	Foreign matters (mm ²)	25	20	20	22
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt.%)		2.1	2.2	1.9	2.1
Particles generated (particles)		20	12	11	10
Etching rate (nm/min)		29	43	25	28

*1 XRD: X-ray diffraction

[0099]

(Example 17)

Quartz glass ingot was prepared in the same manner as in Example 13, except for using 700 g of aluminum chloride and 1,500 g of ethanol as the doping material in the place of 700 g of aluminum nitrate and 1,500 g of pure water. Measurements were performed on the resulting quartz glass ingot for the aluminum concentration and the same items as those measured in Example 1. The results are given in Table 5. It has been confirmed from the results in Table 5 that the

product yields excellent resistance against plasma corrosion.

[0100]

(Example 18)

Quartz glass ingot was prepared in the same manner as in
5 Example 13, except for using a solution obtained by dissolving aluminum
in hydrochloric acid at a concentration of 5 wt.% as the doping material
in the place of 700 g of aluminum nitrate and 1,500 g of pure water.
Measurements were performed on the resulting quartz glass ingot for the
aluminum concentration and the same items as those measured in
10 Example 1. The results are given in Table 5. It has been confirmed from
the results in Table 5 that the product yields excellent resistance against
plasma corrosion.

[0101]

(Example 19)

15 Quartz glass ingot was prepared in the same manner as in
Example 13, except for using a solution obtained by dissolving Al
isopropoxide in propanol at a concentration of 30 wt.% as the doping
material in the place of 700 g of aluminum nitrate and 1,500 g of pure
water. Measurements were performed on the resulting quartz glass
20 ingot for the aluminum concentration and the same items as those
measured in Example 1. The results are given in Table 5. It has been
confirmed from the results in Table 5 that the product yields excellent
resistance against plasma corrosion.

[0102]

25 (Example 20)

Quartz glass was prepared in the same manner as in Example 13, except for using a solution obtained by dissolving Al isopropoxide in ethyl silicate at a concentration of 30 % by weight as the doping material in the place of 700 g of aluminum nitrate and 1,500 g of pure water.

- 5 Measurements were performed on the resulting quartz glass ingot for the aluminum concentration and the same items as those measured in Example 1. The results are given in Table 5. It has been confirmed from the results in Table 5 that the product yields excellent resistance against plasma corrosion.

10 [0103]

Table 5

Example No.		17	18	19	20
Production method		Slip	Slip	Slip	Slip
Metallic element compound		Ethanol + AlCl ₃	Hydrochloric acid + aluminum	Propanol + Al iso-propoxide	Ethyl silicate + Al iso-propoxide
State of sample before etching test	Bubbles (mm ²)	20	19	19	20
	Foreign matters (mm ²)	23	17	20	13
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt.%)		2.1	2.3	1.9	1.8
Particles generated (particles)		19	17	10	10
Etching rate (nm/min)		39	43	35	45

*1 XRD: X-ray diffraction

[0104]

(Example 21)

- 15 A solution prepared by dissolving aluminum isopropoxide in propanol was dropped on the surface of a quartz glass jig 200 mm in diameter and 20 mm in thickness, and an alumina film was formed thereon by hydrolyzing the solution together with water in air. The plane of the quartz glass plate having formed the film thereon was fire

polished and baked by using an oxyhydrogen flame to thereby obtain a smooth transparent fused plane. The average aluminum concentration to a depth of 0.1 mm from the surface portion was found to be 15 wt.%, but the average aluminum concentration to a depth of 1 mm was found to be 0.5 wt.%. The average aluminum concentration of the thus formed quartz glass jig was about 2.1 wt.%.
5

[0105]

Measurements were performed for the same items as those of Example 1, and the results are given in Table 6. It has been confirmed from the results in Table 6 that the product yields excellent resistance against plasma corrosion.
10

[0106]

(Example 22)

Quartz glass ingot was prepared in the same manner as in Example 21, except for using a solution prepared by dissolving aluminum isopropoxide in ethyl silicate in the place of the solution prepared by dissolving aluminum isopropoxide in propanol. Measurements were performed on the resulting quartz glass ingot for the aluminum concentration and the same items as those measured in Example 1. The results are given in Table 6. It has been confirmed from the results in Table 6 that the product yields excellent resistance against plasma corrosion.
15
20

[0107]

(Example 23)

25 Quartz glass ingot was prepared in the same manner as in

Example 21, except for using a solution prepared by dissolving zirconium isopropoxide in propanol in the place of the solution prepared by dissolving aluminum isopropoxide in propanol. Measurements were performed on the resulting quartz glass ingot for the zirconium concentration and the same items as those measured in Example 1. The results are given in Table 6. It has been confirmed from the results in Table 6 that the product yields excellent resistance against plasma corrosion.

[0108]

10 (Example 24)

Quartz glass ingot was prepared in the same manner as in Example 21, except for using a solution prepared by dissolving titanium isopropoxide in propanol in the place of the solution prepared by dissolving aluminum isopropoxide in propanol. Measurements were performed on the resulting quartz glass ingot for the titanium concentration and the same items as those measured in Example 1. The results are given in Table 6. It has been confirmed from the results in Table 6 that the product yields excellent resistance against plasma corrosion.

20

25

[0109]

Table 6

Example No.		21	22	23	24
Production method		Coating	Coating	Coating	Coating
Metallic element compound		Propanol + Al iso-propoxide	Ethyl silicate + Al iso-propoxide	Propanol + Zr iso-propoxide	Propanol + Ti iso-propoxide
State of sample before etching test	Bubbles (mm ²)	24	15	18	19
	Foreign matters (mm ²)	24	28	22	18
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt.%)		2.1	2.4	1.4	1.5
Particles generated (particles)		13	8	13	15
Etching rate (nm/min)		43	32	50	32

*1 XRD: X-ray diffraction

[0110]

5 (Example 25)

Quartz glass ingot was prepared in the same manner as in Example 21, except for using a solution prepared by dissolving aluminum nitrate in pure water in the place of the solution prepared by dissolving aluminum isopropoxide in propanol. Measurements were performed on the resulting quartz glass ingot for the aluminum concentration and the same items as those measured in Example 1. The results are given in Table 7. It has been confirmed from the results in Table 7 that the product yields excellent resistance against plasma corrosion.

15 [0111]

(Example 26)

Quartz glass ingot was prepared in the same manner as in Example 25, except for using a solution prepared by dissolving aluminum chloride in ethanol at a concentration of 30 wt.% in the place

of the solution prepared by dissolving aluminum isopropoxide in propanol. Measurements were performed on the resulting quartz glass ingot for the aluminum concentration and the same items as those measured in Example 1. The results are given in Table 7. It has been confirmed from the results in Table 7 that the product yields excellent resistance against plasma corrosion.

[0112]

(Example 27)

Quartz glass ingot was prepared in the same manner as in Example 25, except for using a solution prepared by dissolving aluminum in hydrochloric acid at a concentration of 5 wt.% in the place of the solution prepared by dissolving aluminum isopropoxide in propanol. Measurements were performed on the resulting quartz glass ingot for the aluminum concentration and the same items as those measured in Example 1. The results are given in Table 7. It has been confirmed from the results in Table 7 that the product yields excellent resistance against plasma corrosion.

[0113]

(Example 28)

A disk jig 200 mm in diameter and 25 mm in thickness was prepared by working the quartz glass body produced in Example 1. A layer containing aluminum distributed at a high concentration was formed on the surface of the jig by a method described in Example 21. The average aluminum concentration of the surface to a depth of 0.1 mm was found to be 15 wt.%, but the average aluminum concentration to a

depth of 1 mm was found to be 4.0 wt.%. The average aluminum concentration of the resulting quartz glass jig was found to be was found to be approximately 4.0 wt.%. Measurements were performed on the resulting quartz glass ingot for the same items as those measured in

5 Example 1. The results are given in Table 7. It has been confirmed from the results in Table 7 that the product yields excellent resistance against plasma corrosion.

[0114]

Table 7

Example No.		25	26	27	28
Production method		Coating	Coating	Coating	Verneuil + Coating
Metallic element compound		Pure water + aluminum nitrate	Ethanol + AlCl ₃	Hydrochloric acid + Al	Al ₂ O ₃ 5% propanol + Al iso-propoxide
State of sample before etching test	Bubbles (mm ²)	19	19	24	16
	Foreign matters (mm ²)	24	18	17	29
XRD*1	Foreign matters	None	None	None	None
Concentration of metallic element (wt.%)		2.0	2.1	2.2	4.0
Particles generated (particles)		13	16	17	7
Etching rate (nm/min)		43	34	39	17

10 *1 XRD: X-ray diffraction.

[0115]

(Comparative Example 1)

A 1,000-g portion of quartz powder consisting of particles 500 μm to 100 μm in particle diameter was filled in a carbon casting mold, and

15 was subjected to a heat treatment at 1,800 °C for a duration of 1 hour in vacuum to obtain a transparent glass 100 mm in diameter and 50 mm in height. Measurements were performed on the resulting quartz glass ingot for the same items as those measured in Example 1. The results

are given in Table 8. It has been found from the results in Table 8 that the etching rate is extremely high, and that the resistance against plasma corrosion of the product is poor.

[0116]

5 (Comparative Example 2)

A 900-g portion of quartz powder consisting of particles 500 μm to 100 μm in particle diameter mixed with 100 g of alumina was filled in a carbon casting mold, and was subjected to a heat treatment at 1,800 °C for a duration of 1 hour in vacuum to obtain a transparent glass 100 mm
10 in diameter and 50 mm in height. The aluminum concentration of the product was found to be 2.0 wt%. Bubbles and foreign matters were found to be present in the glass body.

[0117]

Measurements were performed on the resulting quartz glass
15 ingot for the same items as those measured in Example 1. The results are given in Table 8. Table 8 clearly reads that the product not only contains bubbles and foreign matters at high quantity, but also generates particles at a large quantity, and that the product is found unfeasible for use as a jig for silicon wafers. Furthermore, the etching rate is found to
20 be extremely high, and the resistance against plasma corrosion of the product is found to be poor.

[0118]

(Comparative Example 3)

A 690-g portion of quartz particles was mixed with 310 g of Al_2O_3
25 powder, and the resulting mixture was dropped and fused in an

oxyhydrogen flame at a rate of 50 g/min on a target ingot being rotated at a speed of 1 rpm to obtain a quartz glass ingot 200 mm in diameter and 500 liter in volume. The gas condition was set to flow gaseous H_2 at a rate of 200 liter/min and gaseous O_2 at a rate of 100 liter/min. The target ingot was then set inside a volume 300 mm $\times$ 300 mm $\times$ 200 mm high. The gas flow rate for each of the gases was doubled because bubbles and foreign matters generated at a large amount, but no improvement was observed, and with further increase in gas flow rate led to the destruction of the ingot shape.

10 [0119]

On measuring the aluminum concentration of the thus formed ingot by means of fluorescent X ray analysis, the aluminum concentration at the outermost surface portion was found to be 15.0 wt.%, and that for a portion at the depth of 5 mm was found to be 13.0 wt.%. Since gasification of quartz proceeds at the outermost surface, it is presumed that the concentration tends to become higher at the surface.

[0120]

Measurements were performed for the same items as those measured in Example 1, and the results are given in Table 8. Table 8 clearly reads that, although the etching rate is low, the product not only contains bubbles and foreign matters at high quantities, but also generates particles at a large quantity, and that the product is unfeasible for use as a jig for silicon wafers.

25

[0121]

Table 8

Comparative Example No.		1	2	3
Production method		Vacuum furnace	Vacuum furnace	Verneuil
Metallic element compound		None	Al ₂ O ₃ 5 wt.%	Al ₂ O ₃ 31 wt.%
State of sample before etching test	Bubbles (mm ²)	20	280	449
	Foreign matters (mm ²)	14	538	894
XRD*1	Foreign matters	None	Present	Present
Concentration of metallic element (wt.%)		0.0	2.0	13.0
Particles generated (particles)		20	300	800
Etching rate (nm/min)		120	64	43

*1 XRD: X-ray diffraction

[0122]

5 The content of bubbles and foreign matters in Examples 1 to 28 and Comparative Examples 1 to 3 above was measured in the following manner. Samples 50 mm × 50 mm × 1 mm (thickness) in size were each cut out from the quartz glass bodies, and the both surface planes were mirror polished. Then, white light was allowed to pass from the lower
10 plane of the sample, and the projected images of the bubbles and foreign matters were subjected to image analyzer to count up the quantity of bubbles and foreign matters having a diameter of 0.02 mm or larger. From the thus obtained results, the area (projected area) of the bubbles and foreign matters present in the whole area of the sample were
15 calculated to obtain the cross section area (projected area) per 100 cm².

[0123]

The etching rate was measured in the following manner. From the prepared transparent quartz glass, a sample was cut out and worked to a piece 30 mm in diameter and 3 mm in thickness, and the surface

thereof was fire polished. The sample piece was then subjected to an etching test using a plasma gas containing CF_4 and O_2 (20 %) flown at a rate of 50 sccm under a pressure of 30 mTorr, a power of 1 kW, and for duration of 10 hours. From the weights obtained before and after the test, the change in thickness was calculated, and the calculated result was further divided by the process time to calculate the etching rate.

[0124]

The quantity of generated particles was obtained by mounting a Si wafer having the same area as that of the sample on the plasma-irradiated surface of the sample after etching, and the irregularities on the contact plane of the wafer were detected by laser scattering. Thus, particles 0.3 μm or larger in size were counted up by using a particle counter.

[0125]

In Examples 1 to 28 and Comparative Examples 1 to 3, it was found that the usable portion of the Si wafer was 90 % or higher in case the quantity of generated particles was 50 counts or less, but the yield was greatly reduced to 50 % or lower in case the quantity of generated particles exceeded 200 counts. In case the etching rate was 100 nm/min or higher, the etching thickness resulted in 0.6 mm or more for a use of about 100 hours, thereby making it unfeasible as a member; but with an etching rate of 50 nm/min or lower, the usable duration was doubled to confirm the effect. In particular, an etching rate of 20 nm/min or lower resulted to provide a considerably high economical effect.

[0126]

(Example 29)

A 28,500-g portion of quartz particles consisting of particles from 100 to 500 μm in particle diameter was mixed with 1,500 g of Al_2O_3 powder, and the resulting mixture was dropped and fused in an oxyhydrogen flame at a rate of 50 g/min on a target ingot being rotated at a speed of 1 rpm to obtain a quartz glass ingot of 200 mm in diameter and 400 mm in length. The gas condition was set as such to flow gaseous H_2 at a rate of 300 liter/min and gaseous O_2 at a rate of 100 liter/min.

10 [0127]

The ingot thus prepared was then set inside a heating furnace, and was kept at 1,800 $^{\circ}\text{C}$ for a duration of 2 hours under gaseous N_2 atmosphere at a pressure of 1 kg/cm^2 to obtain a shaped body of 400 mm in diameter and 100 mm in length. A quartz glass disk of 350 mm in diameter and 20 mm in thickness was cut out from the thus obtained quartz glass shaped body, and the upper and the bottom planes were subjected to a cutting. The surface Ra value was found to be 2.0 μm , and the quartz glass disk was found to contain OH at a concentration of 300 ppm.

20 [0128]

Further, qualitative and quantitative analysis of the evolved gas was performed in the temperature range of from room temperature to 1,000 $^{\circ}\text{C}$ on the sample cut out from the same quartz glass shaped body obtained above. As a result, it was found that gaseous CO , H_2O , O_2 , and H_2 were generated in total amount of 0.4 mol/m^3 . The bubbles and

foreign matters inside the quartz glass disk amounted to 10 mm² per 100 cm³, and the internal transmittance of the visible radiation was found to be 85 %/cm.

[0129]

5 The Al concentration as obtained by means of fluorescent X-ray analysis was 3.0 wt.%. A sample of 30 mm in diameter and 3 mm in thickness was cut out, and the surface thereof was subjected to cutting to result in a surface roughness Ra of 2.0 μm. Then, an etching test was performed on the resulting sample in gaseous plasma of CF₄ and O₂
10 (accounting for 20 %) flown at a rate of 50 sccm, under a pressure of 30 mTorr and a power of 1 kW for time duration of 10 hours. The etching rate was calculated from the change of mass before and after the test to obtain a result of 30 nm/min.

[0130]

15 The quantity of generated particles was obtained by mounting a Si wafer having the same area as that of the sample on the plasma-irradiated surface of the sample after etching, and the irregularities on the contact plane of the wafer was detected by laser scattering. Thus, particles 0.3 μm or larger in size were counted up by
20 using a particle counter to obtain 10 counts as a result.

[0131]

(Example 30)

Slurry was prepared by mixing 22,500 g of quartz particles from 100 to 500 μm in particle diameter with 6,000 g of pyrolytic silica
25 particles from 0.01 to 4 μm in particle diameter, 2,100 g of aluminum

nitrate, and 4,500 g of pure water. The slurry was dried for 8 days in air at 40 °C, and, after holding the dried slurry in air at 500 °C for 4 hours, heating treatment was applied thereto in vacuum at 1,800 °C for 1 hour to obtain a transparent quartz glass body of 380 mm in diameter and 25 mm in length. A quartz glass disk of 350 mm in diameter and 20 mm in thickness was cut out from the thus obtained quartz glass body, and the upper and bottom planes were subjected to cutting. The surface Ra value was found to be 3.0 μm, and the quartz glass disk was found to contain OH at a concentration of 300 ppm. The Al concentration of the sample cut out in the same manner as above was measured by means of fluorescent X-ray analysis to be 3.0 wt% as a result. The other results were found to be the same as those obtained in Example 1.

[0132]

(Example 31)

An aqueous aluminum nitrate solution was applied to the surface of the quartz glass jig of 350 mm in diameter and 20 mm in thickness, and the resulting coated plane was molten by means of oxyhydrogen flame to form a smooth transparent fused surface. The surface Ra value of the thus obtained quartz glass jig was found to be 0.2 μm, and the OH concentration was found to be 300 ppm. The Al concentration of the fused plane of the quartz glass jig was measured by means of fluorescent X-ray analysis to find 5.0 wt.% as a result. The other results were found to be the same as those obtained in Example 1.

[0133]

(Comparative Example 4)

A 30,000-g portion of quartz particles consisting of particles from 100 to 500 μm in particle diameter was mixed, charged in a carbon casting mold, and was subjected to a heat treatment at 1,800 °C for a time duration of 1 hour in vacuum to obtain a transparent quartz glass body of 400 mm in diameter and 100 mm in length. The Al concentration of the sample cut out from the resulting glass body was measured by means of fluorescent X-ray analysis to find 0.0 wt.% as a result. Furthermore, a sample was prepared and plasma etching test was performed in a manner similar to that described in Example 1. The etching rate was found to be 120 nm/min. The other evaluation results were the same as those described in Example 1.

[0134]

(Comparative Example 5)

A 27,000-g portion of quartz particles consisting of particles from 100 to 500 μm in particle diameter was mixed with 300 g of Al_2O_3 powder, and the resulting mixture was charged in a carbon casting mold for a heat treatment at 1,800 °C for a time duration of 1 hour in vacuum to obtain a transparent quartz glass body of 400 mm in diameter and 100 mm in length. Numerous bubbles and foreign matters were observed to be present inside the transparent quartz glass body to yield a projected area per 100 cm^3 of 300 mm^2 . The internal transmittance for a visible radiation was found to be 15 %/cm. The Al concentration of the sample cut out from the resulting glass body was measured by means of fluorescent X-ray analysis to be 5.0 wt% as a result. Furthermore, a sample was prepared in the same manner as in Example 1, and

evaluations similar to those in Example 1 were performed thereon to obtain an etching rate of 64 nm/min and a particle generation amounting to 300 counts.

[0135]

5 (Comparative Example 6)

A 17,000-g portion of quartz particles consisting of particles from 100 to 500 μm in particle diameter was mixed with 1,300 g of Al_2O_3 powder, and a transparent quartz glass body was prepared in the same manner as in Example 1. Numerous bubbles and foreign matters were
10 observed to be present inside the transparent quartz glass body to yield a projected area per 100 cm^3 of 300 mm^2 . The internal transmittance for a visible radiation was found to be 15 %/cm. The Al concentration of the sample cut out from the resulting glass body was measured by means of fluorescent X-ray analysis to be 21 wt% as a result. Furthermore, a
15 sample was prepared in the same manner as in Example 1, and evaluations similar to those in Example 1 were performed thereon to obtain an etching rate of 40 nm/min and a particle generation amounting to 800 counts.

[0136]

20 In Examples 29 to 31 and the Comparative Examples 4 to 6 above, the usable portion of a Si wafer with particle generation of 50 counts or less accounted for 90 % or more, but the yield was lowered to 50 % or less in case the particle generation exceeded 200 counts. Further, in case the etching rate was 120 nm/min or higher, the etching proceeded to a
25 depth of 1.0 mm after using for about 100 hours, and the quartz glass

body was found unfeasible for a member. However, the effect of the invention was confirmed as the etching rate decreased to 50 nm/min or lower because the usable life was doubled. Particularly, a great economical effect was obtained as the etching rate decreased to 20
5 nm/min or lower.

[0137]

As described above, the quartz glass and the quartz glass jig according to the present invention possess great effects when used as a jig material in plasma reaction of semiconductor production processes,
10 since said quartz glass and quartz glass jig have excellent resistance against plasma corrosion, and particularly, against the corrosion of F-based gaseous plasma.

15

What is claimed is:

1. A quartz glass having excellent resistance against plasma corrosion, containing:
a metallic element; and
5 bubbles and foreign matters at an amount expressed by projected area of less than 100 mm^2 per 100 cm^3 .
2. A quartz glass having excellent resistance against plasma corrosion as claimed in Claim 1, wherein the boiling point of said metallic element is higher than that of a Si fluoride.
- 10 3. A quartz glass having excellent resistance against plasma corrosion as claimed in Claim 1 or 2, wherein the concentration of said metallic element is in the range of from 0.1 to 20 % by weight.
4. A quartz glass jig having excellent resistance against plasma corrosion made of the quartz glass as claimed in any one of Claims 1 to 3,
15 comprising a metallic element-containing layer containing 0.1 to 20 % by weight of said metallic element with a thickness of from the surface to a predetermined depth.
5. A quartz glass jig having excellent resistance against plasma corrosion as claimed in Claim 4, wherein the thickness of said metallic
20 element-containing layer is at least 5 mm.
6. A method for producing a quartz glass having excellent resistance against plasma corrosion which is to produce a quartz glass ingot having excellent resistance against plasma corrosion from a quartz powder by means of Verneuil method, comprising the steps of:
25 mixing a powder of a metallic element or a compound thereof



with the quartz powder; and

dropping the heated and fused resulting powder mixture to obtain a quartz glass ingot while heating the surface of the quartz glass ingot to a temperature of 1800 °C or higher.

- 5 7. A method for producing a quartz glass having excellent resistance against plasma corrosion, which is to produce a quartz glass ingot having excellent resistance against plasma corrosion from a quartz powder by means of Verneuil method, comprising the steps of:

preparing a quartz glass ingot by dropping the heated and fused
10 quartz glass powder; and

at the same time dropping continuously on the growing surface of said quartz glass ingot, a solution prepared by dissolving a metallic element or a compound thereof in pure water, an acidic solution, an alkaline solution, or an organic solvent.

- 15 8. A method for producing a quartz glass having excellent resistance against plasma corrosion, comprising the steps of:

allowing to stand still a previously prepared porous SiO₂ body;
and

heat-treating it in an atmosphere containing the metallic element
20 at a density in a range of from 0.1 to 10 mol per 22.4 liter.

9. A production method as claimed in Claim 8, wherein said heating temperature is set at a temperature not lower than the boiling point, the gasification point, or the decomposition point, of said metallic element or the compound thereof, and said pressure of treatment is in a range of
25 from 1 to 10 atoms.



10. A method for producing a quartz glass having excellent resistance against plasma corrosion, comprising the steps of:
- preparing a slurry by dissolving in pure water, an acidic solution, an alkaline solution, or an organic solvent, a mixture of a quartz glass powder having a particle size distribution in the range of from 0.01 to 1,000 μm and containing from 1 to 50 % by weight of particles with their size ranging from 0.01 to 5 μm , with a metallic element or a compound thereof soluble in pure water, an acidic solution, an alkaline solution, or an organic solvent;
- 10 drying and solidifying said slurry; and
- then heating and fusing the solidified slurry in vacuum.
11. A method for producing a quartz glass having excellent resistance against plasma corrosion as claimed in Claim 10, wherein said metallic compound is a nitrate compound and the solvent is pure water.
- 15 12. A method for producing a quartz glass jig having excellent resistance against plasma corrosion, comprising the steps of:
- coating the surface of a previously prepared quartz glass jig with a solution prepared by mixing and dissolving in pure water, an acidic solution, an alkaline solution, or an organic solvent, a metallic element or a compound thereof soluble in pure water, an acidic solution, an alkaline solution, or an organic solvent; and
- 20 thereafter by heating and fusing the thus coated surface.
13. A production method as claimed in Claim 12, wherein said solution containing said metallic element is a liquid organometallic compound containing the metallic element, or a solution prepared by
- 25



dissolving the same in an organic solvent.

14. A production method as claimed in Claim 12 or 13, wherein said previously prepared quartz glass jig is produced by one of the production methods as claimed in any one of Claims 6 to 11.

5 15. A quartz glass having excellent resistance against plasma corrosion, containing:

a metallic element; and

bubbles and foreign matters at an amount as expressed by projected area per 100 cm³ of less than 100 mm²; and

10 an OH at a concentration of from 100 to 2000 ppm,

which quartz glass has a surface roughness Ra of 0.01 to 10 μm, and a gas evolution of 2 mol/m³ or less in a temperature range of from room temperature to 1000 °C.

16. A quartz glass having excellent resistance against plasma
15 corrosion as claimed in Claim 15, wherein the metallic element is at least one selected from the group consisting of Sm, Eu, Yb, Pm, Pr, Nd, Ce, Tb, Gd, Ba, Mg, Y, Tm, Dy, Ho, Er, Cd, Co, Cr, Cs, Zr, Al, In, Cu, Fe, Bi, Ga, and Ti.

17. A quartz glass having excellent resistance against plasma
20 corrosion as claimed in Claim 15 or 16, wherein the concentration of the metallic element is in the range of from 0.1 to 20 % by weight.

18. A quartz glass having excellent resistance against plasma
corrosion as claimed in any one of Claims 15 to 17, wherein the internal transmittance for a visible radiation of said quartz glass is 50 %/cm or
25 higher.



19. A quartz glass jig having excellent resistance against plasma corrosion made of the quartz glass as claimed in any one of Claims 15 to 18, including a metallic element-containing layer containing 0.1 to 20 % by weight of said metallic element with a thickness of from the surface to
5 a predetermined depth.
20. A quartz glass jig having excellent resistance against plasma corrosion as claimed in Claim 19, wherein the thickness of said metallic element-containing layer is at least 5 mm.
21. A quartz glass jig having excellent resistance against plasma
10 corrosion as claimed in Claim 19 or 20, wherein at least a surface that is in contact with a plasma corrosive gas is subjected to a precision cutting treatment, a heating and melting treatment, or a heating and melting treatment followed by a chemical etching treatment.

