DESCRIPTION

SILICA GLASS JIG USED IN PROCESS FOR MANUFACTURING SEMICONDUCTOR AND METHOD OF MANUFACTURING SILICA GLASS JIG

Technical Field

The present invention relates to a silica glass jig used in a process for manufacturing a semiconductor, and more specifically, to a silica glass jig that has fine irregularities on a surface and exhibits little change in a surface state against slight surface layer etching, and to a method of manufacturing the same.

Background Art

A silica glass jig has been used in various processes such as a diffusion process, a vapor phase growth process, an etching and ashing processes in manufacturing a semiconductor device. A surface of the silica glass jig is subjected to treatments such as sandblast and grinding working to form an opaque finish with irregularities, or subjected to mirror polishing or flame polishing that is called bake finishing to form a smooth and transparent finish. These finishes are appropriately selected depending on applications, and the jigs frequently used are those having a surface that is finished as a transparent surface that is easy in cleaning and is hardly get spoiled. In a diffusion process and a vapor phase growth process, particularly in the vapor phase growth

process, for example, a polysilicon film is deposited on a semiconductor device by CVD (Chemical Vapor Deposition) or the like. During the deposition, a polysilicon film is deposited as a by-product on a silica glass jig with a transparent finish as well. The polysilicon film may be peeled off the silica glass jig to form particles to contaminate a semiconductor device. Therefore, it is necessary to periodically remove a by-product. A solution containing hydrofluoric acid and nitric acid is typically used for removing the by-product. However, the smooth surface of the jig is also etched at the same time as the removal of the by-product, thereby forming a rough surface. This is a problem in that a surface state such as a surface area is changed; the amount of deposition of a by-product is suddenly changed; the consumption of a vapor phase reaction gas to be consumed is changed; and the control of the amount of growth of a polysilicon film on a semiconductor device becomes difficult. Alternatively, it has been attempted to form fine irregularities on a surface of a jig by sandblast working and prevent generation of particles by positively capturing a by-product in the irregularities. However, in this case, fine fragments of silica glass are scattered during use from damaged parts such as a processed plastic layer or microcracks formed during processing of fine irregularities, generating particles that contaminate a semiconductor device. Moreover, when the thickness of a by-product is increased, breakage due to the difference of thermal expansion between silica glass

and polysilicon may occur. In order to prevent the breakage, cleaning by gas etching or wet etching has been conducted before using a jig. However, it is necessary to periodically remove a by-product in the manner similar to the case of a jig having a transparent surface, and this may cause a problem of simultaneously etching the surface with fine irregularities, changing a surface state.

Above-described problems are observed on a semiconductor device not only in a diffusion process and a vapor phase growth process but also in an etching treatment. That is, also in a process in which etching or ashing is conducted utilizing plasma while flowing a treatment gas, a by-product may deposit on a silica glass jig and is peeled off to generate particles. In such a case, similar to CVD or the like, it has been attempted to form fine irregularities on a surface by sandblast or grinding working to positively capture a by-product to prevent the generation of particles. However, this is a problem in that fine fragments of silica glass are scattered by plasma during use from damaged parts such as a processed plastic layer or microcracks formed during processing of irregularities, generating particles that contaminate a semiconductor device. Particularly, in dry etching, a surface of a silica glass jig has been also etched in the manner very similar to a treatment with a hydrogen fluoride-containing solution. This is a problem in that a surface state was significantly changed and the control of the etching treatment itself of a semiconductor device becomes difficult.

In order to solve the above-described problems, there have been proposed a silica glass jig in which a jig subjected to mechanical working is etched by a hydrogen fluoride-containing solution to open microcracks to form a microcrack-free surface (Japanese Patent Laid-Open No. 10-59744), and a silica glass jig in which a surface of a silica glass jig is made irregular by mechanical working and then treated with a solution containing hydrogen fluoride and ammonium fluoride to form dimple-like depressions of from 20 to 300 μm and grooves of from 0.5 to 50 μm in width spaced apart by 20 to 30 μm, and also small projections of from 1 to 50 μm in width and from 0.1 to 10 μm in height are uniformly dispersed between and within the grooves (Japanese Patent Laid-Open No. 2002-104843). However, both of the above-described jigs have disadvantages in actual use in that the depressions are changed to large cone-shaped depressions by the use of the jigs, suddenly changing the amount of deposition of a by-product, or irregularities are reduced, generating peeled particles after using them continuously for a certain period of time.

As a result of intensive investigations under these circumstances, the present inventors have found that when a silica glass jig has a surface roughness with center line average roughness Ra of from 0.1 to 20 μm and has a surface that exhibits little change in a surface state against slight surface layer etching, peeling of a by-product and scattering of fine fragments of silica glass are eliminated, and a change

in the consumption of a treating gas is low and so the treatment in each process can be easily controlled. Furthermore, it has also been found that the above-described silica glass jig can be easily manufactured by alternately repeating a specified physical surface layer removal means and a specified chemical surface layer removal means two or more times, leading to the accomplishment of the invention.

An object of the present invention is to provide a silica glass jig in which particles to contaminate a semiconductor device are not generated when the jig is used and treatment conditions need not be changed even if the jig is repeatedly used.

Another object of the present invention is to provide a method of manufacturing the above-described silica glass jig.

Disclosure of the Invention

The present invention relates to a silica glass jig used in a process for manufacturing a semiconductor, characterized in that the silica glass jig has irregularities with center line average roughness Ra of from 0.1 to 20 μm on a part or all of a surface thereof and exhibits little change in a surface state on a slight surface layer etching treatment.

The silica glass jig of the present invention is a jig used in a process for manufacturing a semiconductor device, for example, a core tube, a wafer-mounting boat, chambers for etching and ashing and the like. A part or all of a surface

of the silica glass jig has irregularities with center line average roughness Ra of from 0.1 to 20 μm and exhibits little change in a surface state against a slight surface layer etching treatment. The degree of change in the surface state after the slight surface layer etching treatment is preferably 50% or less with the rate of change of center line average roughness, when the surface is etched with a hydrofluoric acid solution in a concentration range of from 3.0 to 4.0% at a solution temperature of from 17 to 23°C for 15 to 17 hours, and the etched surface and the surface before etching are measured for center line average roughness according to JIS B 0601 by a stylus surface roughness measuring instrument in which the tip of a stylus has an R of from 2 to 10 μm. That is, the surface of a silica glass is changed by actual etching, for example, etching by a plasma gas, wherein specifically Ra is increased in the early stage. The degree of the change is related to the rate of change of the center line average roughness indicating the degree of the change in the surface state, and when the rate of change is 50% or less, the change of Ra remains little in actual use as well. When the concentration of the above-described hydrogen fluoride solution is less than the above-described range, the etching is not efficient since it takes too much time to provide the change. When the concentration is above the above-described range, the speed of change in the early stage may be high, reducing the time for determination. However, an error will be generated after the object is taken out of the solution

before the surface thereof is replaced with water to stop etching. Further, the temperature of the hydrogen fluoride solution of from 17 to 23°C is employed since this temperature range is most typically used.

Moreover, the time for an etching treatment of from 15 to 17 hours is the time required for obtaining the rate of change that allows high accuracy for determination. It is important to use a stylus surface measurement instrument in which the tip of a stylus has an R of from 2 to 10 μm according to JIS B 0601 for the measurement of the above-described rate of change. The reason why the above-described stylus surface measurement instrument in which the tip of a stylus has an R of from 2 to 10 μm is used will be described below. The surface state of a silica glass jig is significantly changed during actual use by the etching treatment such that microcracks existing in the surface in the initial stage are enlarged by the etching treatment or the shape of the irregularities with indented notches on the surface are changed by the etching treatment. A non-contact instrument, for example, an instrument using a reflected light of laser, can correctly measure the center line average roughness calculated from the measured shape. However, it is difficult to determine a significant change of state by which the treatment conditions should be changed during use, since the non-contact instrument detects narrow valleys as well that will soon be buried by a by-product while the jig is used. Use of a measurement method using the stylus surface measurement instrument allows easily

capturing the change in projections, and especially in valleys that are sensitive to a situation of by-product deposition. The tip of the stylus has an R of from 2 to 10 μm as described above. This range spans from 2 μm where narrow valleys are not detected to 10 μm where substantial irregularities can be determined. This range can easily measure the change in the surface state corresponding to that in the actual use.

When a silica glass jig is actually used, the amount of a by-product to be captured must be appropriate depending on the process to be used. For example, in the case of the CVD process, roughening the surface of the jig allows an excessive gas from the film growth on a wafer to be captured and deposited in a larger amount on the silica glass jig as a by-product. Also, in the case of the dry etching process by plasma or the like, roughening the surface of the jig allows a reaction gas from the etching to be captured and deposited in a larger amount on the silica glass jig as a by-product. If the amount of deposition of the by-product is too large, the gas for forming a film on a wafer is reduced to a level that is excessively low, inhibiting the growth of the film or etching. On the other hand, if the amount of by-product captured is too small, particles will be generated due to peeling or the like, and the roughness and state of the silica glass jig are changed from the initial state by etching when the jig is used, which proposes a similar problem as described above. The irregularities on a surface of a silica glass jig may be sawlike irregularities, or notches in which irregular, acute peaks

and valleys are contiguously formed, or a series of projections of a trapezoidal shape. All of these irregularities will form cup-shaped irregularities with sharp edges by the etching treatment during actual use, and the capability to capture a by-product and the like will be changed significantly from the initial state. Moreover, when cup-shaped irregularities are formed from the initial state, the capability to capture a by-product will be too small for the actual use as the surface area is small, and a sharp part at the edge of the cup-shape will be dropped off to generate particles. Therefore, the silica glass jig of the present invention has a surface with irregularities of from 0.1 to 20 μm with center line average roughness Ra formed on a part or all thereof. The presence of the irregularities can securely capture a by-product and can suppress the peeling of a film.

Preferably, the above-described irregularities have a multiple structure consisting of large irregularities and fine shallow cup-shaped depressions formed on the surface thereof. This multiple structure can securely capture the by-product of a necessary thickness by large wavy irregularities that are insensitive to slight etching.

Furthermore, fine shallow cup-shaped irregularities formed on the large wavy irregularities can fix the captured by-product without peeling. Thus, a jig with a stable surface can be obtained. Most desirably, the shallow cup-shaped depression has a smaller bottom depth than the edge-level diameter thereof and the edge at the boundary of adjacent

depressions is not acutely convex. Even if the depression is etched during use, the vicinity of the edge is equally worn out due to the above structure, and projected edge that is acute and may be easily fallen off can be prevented from occurring between adjacent depressions.

The silica glass jig of the present invention can be manufactured by repeatedly applying a physical surface layer removal means and a chemical surface layer removal means alternately twice or more. A treatment condition to be preferably selected is a condition where the surface roughness formed by the physical surface layer removal means is successively smaller.

The above-described physical surface layer removal means includes a grinding treatment with a bonded abrasive grain grindstone, a polishing treatment with free abrasive grains, a blast treatment with free abrasive grains, a treatment with liquid honing or combinations thereof. Specifically, the bonded abrasive grain grindstone includes a resin bond diamond grindstone and the like; the free abrasive grain includes silica and SiC; and the treatment with liquid honing includes a treatment in which the free abrasives are dispersed in a liquid for spraying. This physical surface layer removal means forms a damage layer such as a processed plastic layer and microcracks on a surface of a silica glass, which causes generation of particles by scattering fine fragments of silica glass when the jig is used. In addition, heterogeneous erosion occurs during an etching treatment process, leading to

formation of deep grooves due to imperfect opening of microcracks and a significant change in the surface state. Thus, it is necessary to change treatment conditions for a CVD process, an etching process and the like. However, application of a chemical surface layer removal means following the above-described physical surface layer removal means allows removal of the processed plastic layer and opening of the microcracks, reducing the generation of particles and the change in the surface state. However, if the amount of the surface layer removed by the chemical surface layer removal means is small, the removal of the processed plastic layer and the opening of the microcracks will not be sufficient. On the other hand, if it is attempted to sufficiently remove the damage layer containing the processed plastic layer and microcracks formed by the physical surface layer removal means, large grooves and cup-shaped or bowl-shaped depressions with sharp peripheral edges will be formed in large numbers.

Fine glass fragments are likely to be scattered especially from sharp parts at peripheral edges. There is a treatment method described in Japanese Patent Laid-Open No. 2002-104843 as a treatment method in which depressions with the above-described sharp edges are not formed. However, the method described in the patent cannot remove the damage layer such as a processed plastic layer and microcracks formed by the physical surface layer removal means and the surface state during the etching treatment varies significantly. Further, when etching proceeds during actual use, numbers of depressions

with sharp peripheral edges are formed, facilitating generation of particles.

In the manufacturing method of the present invention, the chemical surface layer removal means after the first physical surface layer removal means forms a surface in which microcracks on the surface are opened, for example, a surface in which there are numbers of bowl-shaped or cup-shaped irregularities. Then, the physical surface layer removal means is applied again to convert the acute parts in the irregularities to wavy shapes. Furthermore, the chemical surface layer removal means is applied again to open a processed plastic layer remaining on a relatively flat surface and a small number of remaining microcracks. Preferably, the above-described physical surface layer removal means and chemical surface layer removal means are repeatedly applied alternately twice or more. This provides a silica glass jig in which the change of a surface state of the jig during use is small. More preferably, the above-described physical surface layer removal means is selected such that the surface roughness provided by the next physical surface layer removal means is smaller than that provided by the previous physical surface layer removal means. Thus, the next chemical surface layer removal means can easily open only the damage and microcracks formed by the final application of the physical surface layer removal means without significantly changing the shape of already formed large wavy irregularities, as well as a multiple structure with numbers of cup-shaped depressions

on the surface of large wavy irregularities can be formed. For example, abrasive grains with a relatively large particle size are used first, and abrasive grains with a relatively small particle size are used as the next removal means. In this case, there may be adopted a combination of the physical surface layer removal means in which the grinding treatment with a bonded abrasive grain grindstone is combined with the following polishing treatment with free abrasive grains. For example, a bonded abrasive grain grindstone comprising a diamond abrasive grains of #120 is first used, and then a sandblast treatment with SiC free abrasive grains of #600 is applied.

The chemical surface layer removal means used in the present invention includes a treatment with a hydrogen fluoride-containing solution. Preferably, the chemical surface layer removal means after the last physical surface layer removal means further contains ammonium fluoride in the above-described solution. Although a mechanism is not clear, this allows to remove, for example, sharp projections created on peripheral edges of cup-shaped or bowl-shaped depressions formed by the chemical surface layer removal means and other acute projections, forming a surface with smooth irregularities. This is assumed that the crystals formed by the reaction of hydrogen fluoride and ammonium fluoride with silica often occur, for example, at the bottom of cup-shaped depressions and do not occur at the projections, or the crystals that have absorbed the projections immediately leave the

projections, resulting in selective etching and removal of the projections to form a round shape without acute parts. More preferably, fine particles with a particle size of from 10 to 200 μm of any one selected from the group consisting of a resin, silica and a ceramic, or a combination thereof are dispersed in the above-described hydrogen fluoride-containing solution. By dispersing the fine particles, the damage layer on a surface of a jig can easily be removed; the capability to form fine irregularities is enhanced; and a manufacturing procedure can be simplified. Addition of ultrasonic vibration and agitation means can further enhance the efficiency of the treatment.

The silica glass jig of the present invention generates few particles when the jig is used, and treatment conditions are not almost changed even if the jig is repeatedly used. Thus, it is effective in allowing a treatment of high quality semiconductors with stability. Moreover, the above-described silica glass jig can be easily manufactured by repeatedly applying a specific physical surface layer removal means and chemical surface layer removal means twice or more, and the industrial value thereof is high.

Brief Description of the Drawings

Figure 1 is a photograph of 500 magnifications of the surface of the jig for dry etching in Example 1 observed by a microscope;

Figure 2 is a photograph of 500 magnifications of the surface of the jig for dry etching in Example 1 observed by a microscope after the jig is immersed in hydrofluoric acid of 3.5% by mass for 16 hours;

Figure 3 is a photograph of 500 magnifications of the surface of the jig for dry etching in Example 1 observed by a scanning electron microscope;

Figure 4 is a photograph of 200 magnifications of the wafer boat in Example 2 observed by a scanning electron microscope;

Figure 5 is a photograph of 1,000 magnifications of the wafer boat in Example 2 observed by a scanning electron microscope;

Figure 6 is a photograph of 200 magnifications of the wafer boat in Example 2 observed by SEM after the boat is subjected to the etching test with a hydrofluoric acid solution of 3.5% at 20°C for 16 hours;

Figure 7 is a photograph of 1,000 magnifications of the wafer boat in Example 2 observed by SEM after the boat is subjected to the etching test with a hydrofluoric acid solution of 3.5% at 20°C for 16 hours;

Figure 8 is a photograph of 200 magnifications of the wafer boat in Comparative Example 2 observed by SEM;

Figure 9 is a photograph of 1,000 magnifications of the wafer boat in Comparative Example 2 observed by SEM;

Figure 10 is a photograph of 200 magnifications of the wafer boat in Comparative Example 2 observed by SEM after the

boat is subjected to the etching test with a hydrofluoric acid solution of 3.5% at 20°C for 16 hours; and

Figure 11 is a photograph of 1,000 magnifications of the wafer boat in Comparative Example 2 observed by SEM after the boat is subjected to the etching test with a hydrofluoric acid solution of 3.5% at 20°C for 16 hours.

Best Mode for Carrying Out the Invention

Next, the present invention will be described with reference to Examples, but the present invention is not limited thereto. Incidentally, the center line average roughness Ra in the following Example 1 and Comparative Example 1 was measured with a surface roughness tester (Surfcom 300B available from Tokyo Seimitsu Co., Ltd.). In other Examples and the like, a surface roughness tester available from Mitutoyo Corporation (SJ-400) was used.

Example 1

A surface of a silica glass with a diameter of 300 mm was ground with a resin bond grindstone containing diamond abrasive grains of #300 to prepare a disc-form jig for dry etching. The resulting jig had a center line average roughness Ra of 1.2 μm. The jig was immersed in a hydrofluoric acid solution of 50% for 10 minutes. The resulting jig had a center line average roughness Ra of 2.8 μm. Successively, the jig was subjected to surface removal by a resin bond grindstone composed of SiC abrasive grains of #1,000 to create a center line average roughness Ra of 0.5 μm. The resulting jig was

further treated with a liquid consisting of 15% by mass of hydrogen fluoride, 15% by mass of ammonium fluoride, 50% by mass of acetic acid and water for 1 hour, obtaining a center line average roughness Ra of 1.4 μm. The above-described jig was immersed in a hydrofluoric acid solution of 3.5% by mass at 20°C and examined for the change of Ra. The result is as shown in Table 1. A photograph of the surface at zero hour observed by a microscope is shown in Figure 1; and a photograph of the surface after the etching treatment of 16 hours observed by a microscope is shown in Figure 2. Furthermore, a photograph observed by a scanning electron microscope at zero hour is shown in Figure 3.

Comparative Example 1

A silica glass jig similar to that in Example 1 was ground with a resin bond grindstone containing diamond abrasive grains of #300 to prepare a disc-form jig for dry etching. The resulting jig had a center line average roughness Ra of 1.2 μm. The jig was then immersed in a hydrofluoric acid solution of 10% for 10 minutes, obtaining Ra of 1.3 μm. The jig was examined for the change in surface roughness by hydrofluoric acid of 3.5% by mass in the same manner as in Example 1. The result is as shown in Table 1.

[Table 1]

		0 hour	4 hours	8 hours	16 hours
Example 1	Ra	1.4 μm	1.8 μm	1.9 μm	1.9 μm
	Rate of change	0%	29%	36%	36%
Comparative Example 1	Ra	1.3 μm	1.9 μm	2.8 μm	3.3 μm
	Rate of change	0%	46%	115%	130%

As shown in Table 1 above, the silica glass jig of the present invention in Example 1 exhibited an extremely smaller change in the surface states such as Ra than that in Comparative Example 1, in the etching test with a hydrofluoric acid solution of 3.5% by mass. The jigs from Example 1 and Comparative Example 1 were actually used in a plasma dry etching apparatus of 2 kw with a CF_4/Ar gas. The jig from Example 1 was used for the treatment of 5 batches, and it was observed that generation of particles for each batch was below 10 in number. On the other hand, the jig from Comparative Example 1 showed generation of a large number of particles of 50 or more at the 3rd batch, and the use of the jig was suspended. Moreover, the Ra after use was 2 μm for the jig from Example 1 and 5.2 μm for the jig from Comparative Example 1. This result shows a large difference similar to that in the etching test with a hydrofluoric acid solution of 3.5% by mass. In addition, the etching rate of a treated wafer was compared between the 5th batch from Example 1 and the 3rd batch from Comparative Example 1. It was observed that the jig from Comparative Example 1 showed a lower rate than that from Example 1.

Example 2

A vertical wafer boat for vapor phase growth corresponding to a silicon wafer of 150 mm in diameter was prepared. The above-described wafer boat was subjected to a sandblast treatment with silicon carbide abrasive grains of #150, followed by a treatment with a hydrofluoric acid solution of 15% for 20 minutes and further followed by a sandblast treatment with silicon carbide abrasive grains of #600. The wafer boat was successively treated with a liquid consisting of 14% by mass of hydrogen fluoride, 12% by mass of ammonium fluoride and water for 1 hour. The surface of the resulting wafer boat was photographed by a scanning electron microscope (SEM). The results are shown in Figures 4 and 5. The wafer boat had a surface roughness of 2.1 μm with the center line average surface roughness Ra. As shown in Figures 4 and 5, there was observed a multiple structure in which shallow depressions are formed on the surface of large wavy irregularities. The above-described wafer boat was subjected to the etching test with a hydrofluoric acid solution of 3.5% at 20°C for 16 hours. Photographs of the surface of the wafer boat after the test taken by SEM are shown in Figures 6 and 7. A multiple structure was still observed, in which there were reduced numbers of slightly wider depressions of a larger-than-before wavy shape. The Ra at this time was 2.1 μm. Furthermore, the above-described wafer boat was used in the actual vapor phase growth process of silicon nitride to deposit a film of 2 μm. At every cumulative deposition in the above-described growth process, cleaning with a hydrofluoric acid solution of 4% for

1 hour was repeated 5 times. The surface after use had a Ra of 2.5 μm.

Comparative Example 2

The wafer boat similar to that in Example 2 was subjected to a sandblast treatment with silicon carbide abrasive grains of #150, followed by a sandblast treatment with silicon carbide abrasive grains of #600. Next, the boat was treated with a hydrofluoric acid solution of 10% for 1 hour. The surface of the resulting wafer boat was photographed by a scanning electron microscope (SEM). The results are shown in Figures 8 and 9. The wafer boat had a roughness with the center line average roughness Ra of 2.2 μm. The above-described wafer boat was subjected to the etching test with a hydrofluoric acid solution of 3.5% at 20°C for 16 hours in the same manner as in Example 2. Photographs of the surface of the wafer boat after the test taken by SEM are shown in Figures 10 and 11. This surface, which was significantly different from the surface in Figure 6 in which large depressions with acute edges are contiguously formed, had an Ra of 4.8 μm. Furthermore, the above-described wafer boat was used in the actual vapor phase growth process of silicon nitride. At every cumulative deposition of a film of 2 μm, cleaning with a hydrofluoric acid solution of 4% for 1 hour was repeatedly performed 5 times. The surface after use had an Ra of 5.1 μm. Moreover, the film thickness growing on the wafer suddenly decreased since the 3rd time, and the increase of particles on the treated wafer was observed.

Industrial Applicability

The silica glass jig of the present invention does not generate particles to contaminate a semiconductor device when the jig is used and treatment conditions need not be changed even if the jig is repeatedly used. Therefore, the silica glass jig of the present invention can be used effectively as a core tube, a wafer-mounting boat, chambers for etching and ashing, a ring, and a plate.

CLAIMS

1. A silica glass jig used in a process for manufacturing a semiconductor, characterized in that the silicon glass jig has irregularities with center line average roughness Ra of from 0.1 to 20 μm on a part or all of a surface thereof and the rate of change of center line average roughness is 50% or less when the surface etched with an aqueous hydrogen fluoride solution in a concentration range of from 3.0 to 4.0 at a solution temperature of from 17 to 23 °C for 15 to 17 hours and the surface before etching were measured according to JIS B 0601 by a stylus surface roughness measuring instrument in which the tip of stylus has an R of from 2 to 10 μm.

2. The silica glass jig according to claim 1, characterized in that a total roughness comprising irregularities of Ra from 0.1 to 20 μm on a part or all of the surface is controlled by a multiple structure composed of large wavy irregularities and fine shallow cup-shaped depressions present on the surface thereof, wherein

each of said cup-shaped depressions has a bottom depth smaller than an edge-level diameter thereof; and wherein

the depressions have a not acutely convex edge formed therebetween.