METHOD FOR PRODUCTION OF SOI SUBSTRATE BY PASTING AND SOI SUBSTRATE

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a method for the production of a pasted SOI substrate and the SOI substrate and more particularly to a method for the production of a pasted SOI substrate which has repressed birth of voids liable to occur particularly in the most peripheral part thereof, widened the area thereof available for the manufacture of devices, increased the number of devices derivable therefrom, and improved yield and the SOI substrate.

Related Background Art

The formation of a single crystal Si semiconductor layer on an insulator is widely known as the "silicon on insulator (SOI)" technique. Many studies have been made on this substrate because the substrate possesses numerous excellent points which are never attained by standard bulk Si substrates for the manufacture of Si integrated circuits.

In the recently reported SOI structures, the so-called "pasted SOI" stands out particularly in terms of quality. This pasted SOI is the product of the technique which comprises preparing two wafers at least either of which has formed an insulating film as by

oxidation, tightly joining the two wafers on the mirror faces thereof, heat-treating the joined wafers thereby fortifying the bondage of the tight interface, and then polishing or etching either of the substrates of the joined wafers until a Si single crystal thin film of an arbitrary thickness remains on the insulating film.

Many studies have been made concerning the mechanism of the pasting which constitutes itself the backbone of this technique. The method for cleaning the two substrates before they are pasted to each other is reckoned as one of the important items of these studies. It has been ascertained to the scientists that the two substrates are first given weak bondage by the Van der Waals force during their contact at room temperature and then given strong interatomic bondage by a subsequent heat-treatment at an elevated temperature. The state of this Van der Waals bondage is widely varied by the method to be used for cleaning the substrates. In Proceedings of 4th International Symposium on Silicon-on-Insulator Technology and devices, May 6-11, 1990, Montreol, for example, Abe et al., regarding the pasting of Si and SiO_2, report "that while the wafers cleaned with a HF solution are bonded only with great difficulty, the wafers which have undergone the so-called "RCA cleaning" are bonded easily because they have formed a spontaneous oxide film on their surfaces". Many other researchers assert

that the water adsorbed to the interface of the pasted substrates plays an important role in the bondage by the Van der Waals force and, therefore, the silicon surfaces are required to be hydrophilic. In Japanese Journal of Applied Physics, Vol. 30, No. 4, April 1991, pp. 615, Mitani et al. report "that the wafer surfaces cleaned by the HF dipping generate more bubbles in the range of annealing temperatures of 200°C - 800°C than the wafer surfaces cleaned by the dipping in NH_4OH + H_2O_2, notwithstanding the former wafer surfaces are inferred to have less -OH groups than the latter wafer surfaces".

It has been consequently held generally that when Si and SiO_2 are pasted, no perfect bondage is obtained unless at least the Si side has undergone a treatment for the impartation of hydrophilicity.

The present inventors, in their experiment which comprises pasting a Si wafer treated to acquire hydrophilicity and a Si wafer provided with an oxide film and heat-treating the pasted wafers, have found that voids considered to have originated in bubbles occur at a high density in the peripheral part of the substrate (in an annular area within about 3 mm - 4 mm from the wafer edge) (hereinafter referred to as "peripheral voids"). The group of voids has the possibility of decreasing the area available for the formation of devices and, at the same time, suffering

the exfoliated fragments of films to adhere to the wafer surfaces and give rise to the problem of hindering the process of device manufacture.

SUMMARY OF THE INVENTION

An object of this invention is to provide a method for the production of a pasted SOI substrate which precludes the occurrence of voids even in the peripheral part of pasted wafers and the SOI substrate.

The method for the production of a pasted SOI substrate of this invention comprises pasting a first Si substrate possessing a SiO_2 surface and a second Si substrate possessing a Si surface on the SiO_2 surface and the Si surface, characterized by the Si surface of the second substrate being vested with hydrophobicity due to a washing treatment before the first substrate and the second substrate are pasted.

The SOI substrate of this invention is further characterized by the presence of Si in the area stretching to 2 mm from the peripheral edge of the substrate and the absence of locally distributed voids in the peripheral part of the substrate.

Now, this invention will be described below.

The excess water adsorbed to the wafer may be cited as one of the causes for the occurrence of voids in the interface of pasting. For the purpose of diminishing such voids, therefore, it becomes necessary

to remove properly the adsorbed water before the substrates are pasted.

As respects the determination of the amount of adsorbed water on the SiO_2 surface, while the amount of adsorbed water is not easily determined immediately after the sample is extracted from purified water, it nearly levels off several minutes to ten-odd minutes after being spin dried. The inventors' experiment with an APIMS device has confirmed this constant amount to be in the approximate range of $0.8 - 1 \times 10^{15}$ molecules/cm^2. It has been further found that this amount varies with the temperature and the humidity of an environment in which the washed wafers are left standing but that it depends very little on the washing method favoring hydrophobicity or hydrophilicity.

It has been also clarified that the amount of adsorbed water on the Si surface indeed depends on the duration of the standing of the sample at rest after the washing treatment but that it depends to a greater extent on the method of washing. When a bare wafer is immersed in HF (an aqueous 1.5% hydrofluoric acid solution), a hydrophobic washing liquid, thoroughly rinsed with purified water, spin dried, and left standing at rest for about 60 minutes, and then tested for the amount of adsorbed water by the use of the APIMS, for example, the amount is found to be about $6 \times 10^{13}/cm^2$. When the same sample is washed with SC-2 (a 1

: 1 : 5 mixture of HCl : H_2O_2 : H_2O), a hydrophilic washing liquid, thoroughly rinsed with purified water, spin dried, left standing at rest for about 60 minutes, and tested for the amount of adsorbed water by the use of the APIMS, the amount is found to be about $3 \times 10^{14}/cm^2$. It is inferred that this difference in the amount of adsorbed water is still larger when the test is made immediately after the spin drying.

When the control of the amount of adsorbed water on the wafer surface is effected by the hydrophobic and hydrophilic methods of washing the Si surface-containing side of the wafer, the conspicuous difference is obtained with high repeatability. Though the control may be attained by such other methods as allowing the washed sample to stand at rest for a prescribed time or giving the washed sample a positive drying in a vacuum, for example, these methods do not offer very high control because they after all rely on the environment in which the pasting is made. Further, the control on the SiO_2 surface-containing wafer side is difficult because the area for control is narrow.

From the results of the studies described above, it is inferred that the conditions for enabling the pasting to proceed without entraining the occurrence in the periphery of wafer of voids of millimeter size considered to originate in the excessive amount of the adsorbed water are (1) that the pasting should take

place on the combination of Si and SiO_2 and (2) that at least the Si side should have undergone the hydrophobic method of washing.

The inventors have also studied the extent to which the amount of the adsorbed water on the Si surface can be controlled exclusively by the method of washing. First concerning the hydrophilic washing for which SC-1 (a mixture of NH_4OH : H_2O_2 : H_2O), H_2SO_4 : H_2O_2, HNO_3, etc. are available in addition to SC-2, it has been found that the amounts of these liquids which remain in the adsorbed state become nearly equal after the washed samples are finally rinsed with purified water. Then, concerning the hydrophobic washing, it has been found that even when the HF is used in a varying concentration or when BHF (a buffered hydrofluoric acid) solution is used instead, the amounts of the liquids remaining in the adsorbed state likewise become nearly equal. The results indicate that intermediate values between the values obtained by the hydrophobic treatment and those obtained by the hydrophilic treatment are difficult to obtain.

In the pasting of a Si and a SiO_2 substrate, the relation between the various methods used for washing and the peripheral voids or the voids, several μm - several hundred μm in diameter (hereinafter referred to as "microvoids"), scattered in the wafer surface is studied. When the two substrates are subjected to a

hydrophilic washing, then pasted, heat-treated at 800°C - 1000°C, and observed by transmission with the aid of an infrared camera, it is found that voids 500, 1 mm through several mm in diameter, inevitably occur along the outer peripheral part of wafer as shown in Fig. 5. In contrast, when the two substrates are subjected to a hydrophobic washing and then pressed against each other in an effort to paste them, they will at times fail to be pasted perfectly if either of the wafers happens to be exposed to stress. This failure may be logically explained by a supposition that the Van der Waals force is not sufficient because of the shortage of water on the surface. They could be pasted if the stress on the wafer was small and the surface was smooth. The peripheral voids are markedly decreased when the conversion of a wafer on one side into a layer of a small wall thickness is carried out after a heat treatment at 800°C - 900°C. In this case, however, microvoids inevitably occur at a density roughly several times through ten-odd times the density observed in the sample which undergoes a hydrophilic treatment. This trouble again may be explained by supposing that the Van der Waals force is not sufficient. When the Van der Waals force is not sufficient, the microgaps which arise in the interface between the two substrates survive all attempts to eliminate them and, consequently, the wafers having

undergone a heat treatment inevitably form an incomplete interface. It is inferred that the polishing which is performed for the conversion of a wafer into a layer of a small thickness exerts on the interface between the pasted substrates such stress as gradually grows in proportion as the polished surface approximates closely to the interface and that the strain consequently generated concentrates on incomplete points and gives rise to the microvoids.

The results of the tests described above, when summarized, lead to the following conclusions: (1) Concerning the amount of water adsorbed to the Si surface, the intermediate value between the hydrophobic treatment and the hydrophilic treatment is not easily obtained. (2) A Si surface, when subjected to hydrophobic washing and pasted with a SiO_2 surface, produces markedly fewer voids than when the Si surface is subjected to hydrophilic washing. (3) The two substrates subjected to hydrophobic washing and pasted have a weak Van der Waals force and tend to generate microvoids as compared with those subjected to hydrophilic washing.

As a result of a further study, it has been found that the microgaps in the interface between the pasted substrates are eliminated by heightening the temperature of the heat treatment. This elimination is logically explained by a supposition that the SiO_2

begins to soften at the same time that the air entrapped in the gaps begins to diffuse. It has been also found that the temperature at which this phenomenon occurs is about 900°C. If the two substrates which have undergone the hydrophilic treatment are used in this case, the microvoids will enlarge conversely because of the collection of the excess water in the form of high-pressure gas in the microgaps. The voids 500 which appear along the outer peripheral part of the pasted wafer illustrated in Fig. 5 exactly the result of this enlargement. It is inferred that these voids occur because the outer peripheral part of wafer has a slightly larger roughness than the central part thereof and because the gas of excess water is not completely diffused through the interface to the exterior. Incidentally, when two SiO_2 substrates are similarly pasted to each other, the same result tend to occur unless the excess adsorbed water is controlled.

From the results of the studies described above, it is evident that the conditions for successfully pasting two substrates without entraining the occurrence of not only voids of millimeter size but also microvoids are (1) that the pasting should take place on the combination of Si and SiO_2, (2) that at least the Si side should have undergone the hydrophobic method of washing, and (3) that the pasted substrates

should then be heat-treated at a temperature of not lower than 900°C.

To be more specific, when the Si and SiO_2 substrates are pasted and then annealed at a low temperature (400°C - 800°C), the density of microvoids is higher in the samples which have undergone a hydrophobic washing than when those which have undergone a hydrophilic washing. In both the two sets of samples, the density of microvoids decreases in accordance as the temperature of heat treatment rises. Under the annealing conditions involving temperatures in the range of 1000°C - 1100°C, the difference nearly ceases to exist between the samples of hydrophilic washing and those of hydrophobic washing.

Concerning the peripheral voids, however, the samples of hydrophobic washing generate no peripheral voids even at high temperatures, whereas those of hydrophilic washing generate peripheral voids in a range from low temperatures through high temperatures. Incidentally, the peripheral voids, unlike the microvoids, do not have their density notably changed (in spite of a slight change in void diameter) by the temperature of heat treatment.

In the formation of devices on a semiconductor substrate, how closely to the peripheral part of the substrate these devices are derived in high yield from the substrate constitutes itself an important factor in

terms of cost. The SOI substrate which is formed by the pasting method, however, has the problem that the Si film tends to shed off the peripheral part thereof. One of the causes for this problem is the occurrence of peripheral voids which is ascribable to the roughness of the periphery of a wafer and the entrapment of water (steam) in that area. The peripheral voids generally occur outside a distance of 5 mm from the peripheral part, though this distance is affected by the conditions of annealing, the magnitude of roughness of the wafer, etc. The area sustaining the peripheral voids, therefore, do not allow formation of devices. Part of the trade advocates a practice of completely removing the peripheral void area of the film itself by photolithographically etching this area before the film is subjected to a process for the formation of devices.

There are times when the formation of devices is not attainable within a distance of about 5 mm from the peripheral edge in spite of the absence of occurrence of peripheral voids.

In the conversion of a wafer into a thin film by polishing, for example, the so-called "film sagging", a phenomenon that the film becomes extremely thin in the peripheral part, inevitably occurs because the polishing rate is larger in the peripheral part of the film than in the central part. Though this problem belongs largely to the performance of the polishing

apparatus being used, it does not easily allow perfect solution. The wafer which is set in place on the polishing apparatus is generally polished by being simultaneously rotated and revolved. During this operation, the sliding speed which the wafer produces relative to the polishing pad varies in the central part and the peripheral part of the wafer surface. In respect exclusively of the rotational motion of the wafer, the sliding speed of the wafer relative to the polishing pad is naturally smaller in the part close to the center than in the outer peripheral part. The difference in the sliding speed results not only in a difference in the amount of sliding motion but also in a difference in the amount of heat to be generated. The amount of the heat thus generated further gives birth to a difference in the polishing rate and aggravates the polishing thickness distribution (film sagging).

The pasted SOI wafer which suffers Si to survive within a distance of 2 mm from the periphery and yet allows the Si surviving peripheral area to manifest characteristic properties favorably comparable with those in the central part regarding the manufacture of devices is not easily manufactured.

The problems described above must be overcome for the purpose of obtaining a SOI thin film which is tightly pasted as far as the distance of 2 mm from the

periphery. Firstly, the pasting must be carried out without entraining the occurrence of peripheral voids. This condition can be accomplished in the pasting of a Si and a SiO_2 substrate by causing at least the Si substrate to be given a hydrophobic washing treatment and then to be heat-treated at a temperature of not lower than 900°C. Secondly, the finishing step in the manufacture of a SOI wafer must be effected by selective etching capable of high selectivity ratio or local plasma etching instead of polishing. By combining these procedures, the SOI wafer in which the Si film survives in a state allowing formation of devices as far as a distance of 2 mm from the periphery can be produced.

By further performing the heat treatment on the two pasted substrates in an oxidizing atmosphere, the tightly joined part is allowed to expand in the peripheral part and the SOI wafer in which the Si film survives as far as 1 mm or even less than 1 mm from the periphery can be produced. An oxidation to be performed subsequently to the heat treatment brings about the same result as the use of the oxidizing atmosphere in the heat treatment.

According to this invention, by pasting a hydrophobic Si substrate and a SiO_2 surface, the bubbles (voids) which are liable to occur particularly in the most peripheral part of the wafer can be repressed, the

area of the most peripheral part available for the manufacture of devices can be widened, the number of devices derivable from the area can be increased, and the yield of the production can be improved.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A, 1B, 1C and 1D are model cross sections illustrating one embodiment of the method of this invention for the formation of a pasted SOI substrate and first and second working examples thereof.

Figs. 2A, 2B, 2C, 2D and 2E are model cross sections illustrating another embodiment of the method of this invention for the formation of a pasted SOI substrate and third working example thereof.

Figs. 3A, 3B, 3C and 3D are model cross sections illustrating yet another embodiment of the method of this invention for the formation of a pasted SOI substrate and fourth working example thereof.

Figs. 4A and 4B are cross sections illustrating the construction of an apparatus for production to be used in the method of this invention for the production of a pasted SOI substrate.

Fig. 5 is a diagram illustrating the image of voids locally present in the wafer periphery which frequently occur in the conventional pasted substrates.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of this invention for the formation of the SOI substrate will be outlined below with reference to Figs. 1A to 1D, Figs. 2A to 2E, Figs. 3A to 3D and Figs. 4A and 4B.

[Fig. 1A] First, a first Si substrate 101 having a surface of SiO_2 (in the diagram, 102 represents a SiO_2 layer) and a second Si substrate 110 having a surface of Si are prepared. As the simplest system of the first Si substrate 101, a Si substrate having an oxidized surface may be exemplified. Another possible system thereof may be a Si substrate having SiO_2 deposited on the surface thereof as by CVD or a multilayer structure having not a Si substrate but a Si layer incorporated therein. As a concrete example of this system, what is obtained by rendering porous the surface or the entire mass of a Si substrate, epitaxially growing a Si single crystal thin film on the porous texture of the Si substrate, and further oxidizing the surface of the Si single crystal thin film may be exemplified. As other concrete examples of the system, what is obtained by epitaxially growing a Si single crystal thin film on a sapphire substrate and further oxidizing the surface of the thin film and what is obtained by oxidizing the surface of a heteroepitaxial substrate or superposing SiO_2 on the surface thereof as by CVD may be cited.

The second Si substrate 110 may be considered as the first Si substrate which has no SiO_2 surface but has a Si surface.

[Fig. 1B] Then, the second Si substrate 110 has the Si surface thereof rendered hydrophobic. The most popular method that is used for rendering the Si surface hydrophobic consists in immersing the surface in a hydrofluoric acid type washing liquid. At this time, the first Si substrate 101 having a SiO_2 surface may be given either a hydrophobic treatment or a hydrophilic treatment. The reason for this indifference as to the kind of treatment is that the SiO_2 surface produces virtually no difference in the amount of adsorbed water in the treatment solely consisting in immersion in a solution as already pointed out.

Then, these two substrates are pasted each other surfaces and the pasted substrates are subsequently heat-treated at a temperature of not lower than 900°C. Though the duration of the heat-treatment is arbitrary, it is several hours at temperatures in the neighborhood of 900°C and several minutes through some tens of minutes at 1200°C.

[Fig. 1C] The resultant integrated substrate is thinned from either of the opposite sides thereof eventually to produce a construction having a Si layer 103 remaining on the SiO_2 (the diagram of Fig. 1C

depicting a case of thinning the first substrate 101). The thickness of the Si layer is arbitrary. The methods available for thinning the integral substrate are broadly divided into the method by polishing and the method by etching. By either of these methods, the thinning is effected efficiently when the greater part of the wall to be removed is ground out. Fig. 1D depicts a case of thinning the second Si substrate 110 and allowing the Si layer 111 to remain.

The polishing method and the etching method have their own merits and demerits. For the manufacture of an extremely thin SOI layer, the selective etching technique can be utilized. The etching method which permits easy control of the film thickness is considered to be slightly advantageous over the polishing method. As one version of the selective etching method, the method for forming a SOI substrate using porous silicon will be described below with reference to Figs. 2A to 2E and Figs. 3A to 3D.

[Fig. 2A] First, a porous Si layer 202 is formed by subjecting a single crystal Si substrate 201 to anodic formation. The thickness of the porous texture to be formed in this case may be several μm through some tens of μm in the surface layer on either side of the substrate. The anodic formation, when necessary, may be effected throughout the entire volume of the substrate. The method for the formation of the porous

Si layer will be described with reference to Figs. 4A and 4B. First, a P type single crystal Si substrate 401 will be prepared as a substrate. An N type equivalent is not unusable. If the equivalent is used, then it will be either limited to low resistance or exposed to a radiation capable of promoting formation of holes in the surface. The substrate 401 is set in place in an apparatus constructed as illustrated in Fig. 4A. Specifically, one side of the substrate contacts a hydrofluoric acid type solution 404, a negative electrode 406 is disposed on the solution side, and a positive metallic electrode 405 contacts the opposite side of the substrate 401. As illustrated in Fig. 4B, a positive electrode side 405' may be endowed with a potential through the medium of a solution 404'. In either of the setups mentioned above, the formation of a porous texture is initiated on the negative electrode side which is in contact with the hydrofluoric acid type solution. Generally concentrated hydrofluoric acid (49% HF) is used as the hydrofluoric acid type solution 404. When the concentrated hydrofluoric acid is gradually diluted with purified water, the acid diluted to a certain concentration induces an objectionable etching action, though depending on the magnitude of an electric current to be passed. During the anodic formation, the surface of the substrate 401 inevitably emits bubbles.

For the purpose of efficiently removing the bubbles, an alcohol may be added as a surfactant. As concrete examples of the alcohol used effectively herein, methanol, ethanol, propanol, and isopropanol may be cited. Instead of using the surfactant, a stirrer may be utilized to stir the solution while the anodic formation is in process. The negative electrode 406 is made of such a material as gold (Au) or platinum (Pt) which is incapable of being corroded by the hydrofluoric acid solution. The positive electrode 405 may be made of any of metallic materials which are commonly used for anodes. The surface of the positive electrode 405 is preferably coated with a metallic film resistant to the hydrofluoric acid solution because the hydrofluoric acid solution 304 reaches the positive electrode 405 by the time that the entire volume of the substrate 401 had undergone the anodic formation. The magnitude of the electric current to be used for performing the anodic formation is some hundreds of mA/cm^2 at the maximum and may assume any value other than 0 as the minimum. This magnitude is set within a range in which perfect epitaxial growth is attained on the surface of a porous Si layer. Generally, the speed of the anodic formation increases and the density of the porous Si layer decreases in accordance as the magnitude of the electric current increases. The volume occupied by the pores proportionately increases.

This volume varies the conditions for the epitaxial growth.

[Fig. 2B] On the porous layer 202 which is formed as described above, a nonporous single crystal Si layer 203 is epitaxially grown. The epitaxial growth is effected by the thermal CVD, reduced-pressure CVD, plasma CVD, molecular-beam epitaxy, and sputtering method which are in common use. The thickness of the epitaxially grown film properly is equal to the design value of the thickness of the active layer.

[Fig. 2C] The first Si substrate is completed by oxidizing (the reference numeral 204 denoting a SiO_2 film) the surface of the epitaxial layer 203 of the substrate obtained by the method described above. A separately prepared Si substrate 210 constitutes itself the second Si substrate.

The thickness of the SiO_2 film of the first Si substrate 201 is arbitrary and is only required to equal the thickness of a buried SiO_2 layer to be designed.

[Fig. 2D] The first substrate 201 mentioned above and the second substrate 210 destined to serve as a support substrate are washed and then pasted together. The method for this washing has only to conform to the standard procedure which is followed in washing a semiconductor substrate (before the step of oxidation, for example) with necessary modifications. It must use

at the final step of washing a washing liquid which imparts hydrophobicity to the Si surface. This washing liquid is a hydrofluoric acid type solution. Incidentally, the first substrate which has a SiO_2 surface it not always required to be finally washed with the hydrofluoric acid type solution.

Then, the integrated substrate obtained by pasting as described above is heat-treated. The temperature of this heat treatment is preferred to be as high as possible. If it is unduly high, however, the porous layer 202 will induce a structural change or the impurity contained in the substrate will undergo diffusion in the epitaxial layer. Thus, the temperature and the duration of the heat treatment are selected so as to preclude such unwanted phenomena. Specifically, the temperature is proper in the approximate range of 900°C - 1100°C.

[Fig. 2E] Subsequently, the Si substrate part 201 and the porous part 202 are selectively removed and the epitaxially grown layer 203 of the first substrate is left behind. First, the Si substrate part 201 is ground with a surface grinder or removed with an alkali solution such as, for example, potassium hydroxide or aqua ammonia or with an organic alkali solution such as, for example, TMAH. By the etching, the removal is effectively attained in a hot solution having a temperature of not lower than 80°C. The polishing or

the etching is terminated provisionally at the time that the porous part 202 is exposed. The exposed porous part 202 is selectively etched by the use of a mixed solution of hydrofluoric acid/aqueous hydrogen peroxide solution or an alkali solution. By appropriately controlling the concentration of the etching liquid, the selectivity ratio of etching between the porous Si layer and the single crystal Si layer can be increased to the approximate maximum of 100,000 : 1. As concerns the liquid concentration, the hydrofluoric acid concentration in the hydrofluoric acid type solution is in the approximate range of several % to several ppm, preferably 0.1% to 10 ppm. As concrete examples of the alkali, ammonia, TMAH (tetramethyl ammonium hydroxide), and ethylene diamine may be cited. The etching with the alkali is preferred to be carried out with the same liquid concentration as in the hydrofluoric acid type solution. For the purpose of enabling the etching liquid to permeate efficiently into the pores of the porous layer, promoting the etching action, and ensuring uniform progress of the etching action, it is advantageous to use an ultrasonic washing device.

Figs. 3A to 3D illustrate another modes of effecting the method for selective etching with a porous Si layer. Fig. 3A depicts the first substrate of this invention which has an oxide film 304 formed on

a Si substrate 310. Fig. 3B represents the second Si substrate of this invention having a porous Si layer 302 and a nonporous Si layer 303 on the Si substrate 301 obtained up to the step of Fig. 2B already explained. The nonporous Si layer 303 is formed by epitaxial growth on the porous Si layer 302. In the modes described with reference to Figs. 2A to 2E, the epitaxially grown substrate is the first Si substrate and the Si substrate is the second Si substrate. In the modes of Figs. 3A to 3D, they are reversed.

Then, the second Si substrate is washed with a hydrofluoric acid type solution so that the Si surface thereof to be used for pasting will acquire hydrophobicity. Thereafter, the SiO_2 surface 304 of the first Si substrate 310 and the Si surface 303 of the second Si substrate 301 are pasted together as illustrated in Fig. 3C to obtain such a SOI substrate as is illustrated in Fig. 3D by adopting the same procedure as explained with reference to Figs. 2A to 2E.

Now, working examples of this invention will be described below.

Example 1:

The first example of this invention will be described below with reference to Figs. 1A to 1D.

[Fig. 1A] Two 5-inch P type single crystal Si substrates (10 Ωcm - 20 Ωcm) having a thickness of

625 μm were prepared. The surface of one of the two substrate was oxidized (oxidized film 102 in the diagram) in a thickness of 0.5 μm. The oxidized side was used as a first Si substrate 101 and the other side which was left unprocessed as a second Si substrate 110.

[Fig. 1B] The two substrates 101 and 110 were washed with a NH_4OH : H_2O_2 : H_2O solution, rinsed with purified water, then washed with a HF : H_2O solution (1.5%), rinsed, spin dried, and pasted together. The pasted substrates were heat-treated at 1050°C for two hours.

[Fig. 1C] The substrate 101 was ground from the first Si substrate 101 side to a depth of 615 μm by the use of a surface grinder. It was subsequently ground to mirror finish with colloidal silica abrasive until the Si film 101 remained in a thickness of 2 μm on the Si oxide film 102, to obtain a SOI wafer.

Microvoids which inevitably occurred in this SOI wafer had diameters in the approximate range of 0.5 μm - 10 μm and a density of about 0.1 piece/cm^2. A comparative sample produced at the same time, with the washing prior to the pasting discontinued at the step using the NH_4OH : H_2O_2 : H_2O solution (the silicon surface rendered hydrophilic), was on a par with the sample of the working example in terms of microvoids but had large voids, several mm in diameter, formed

continuously in an annular pattern in the peripheral part as shown in Fig. 5.

Example 2:

The second working example of this invention will be described below with reference to Figs. 1A to 1D.

[Fig. 1A] Two 5-inch P type single crystal Si substrates (10 Ωcm - 20 Ωcm) having a thickness of 625 μm were prepared. The surface of one of the two substrate was oxidized (oxidized film 102 in the diagram) in a thickness of 0.5 μm. The oxidized side was used as a first Si substrate 101 and the other side which was left unprocessed as a second Si substrate 110.

[Fig. 1B] The two substrates 101 and 110 were washed with a NH_4OH : H_2O_2 : H_2O solution, rinsed with purified water, then washed with a HF : H_2O solution (1.5%), rinsed, spin dried, and pasted together. The pasted substrates were heat-treated at 1200°C for 10 minutes.

[Fig. 1D] The substrate 110 was ground from the second Si substrate side to a depth of 615 μm by the use of a surface grinder. It was subsequently ground to mirror finish with colloidal silica abrasive until the Si film 101 remained in a thickness of 2 μm on the Si oxide film 102, to obtain a SOI wafer.

Microvoids which inevitably occurred in this SOI wafer had diameters in the approximate range of

0.5 μm - 3 μm and a density of about 0.1 piece/cm^2. A comparative sample produced at the same time, with the washing prior to the pasting discontinued at the step using the NH_4OH : H_2O_2 : H_2O solution (the silicon surface rendered hydrophilic), was on a par with the sample of the working example in terms of microvoids but had voids, though averaging in reduced diameters of several hundreds of μm as compared with the comparative sample of Example 1, remaining in an annular pattern just the same.

Example 3:

[Fig. 2A] A 5-inch single crystal P type Si substrate (0.01 Ωcm - 0.02 Ωcm) 201 having a thickness of 625 μm was prepared, set in place in such an apparatus as illustrated in Fig. 4A, and subjected to anodic formation to have the surface of the Si substrate 201 converted into a porous Si layer 202 in a thickness of 20 μm. For the anodic formation, a 49% HF solution was used as the solution 304 and the current density was set at 1 mA/cm^2. The formation of the porous texture proceeded at a rate of about 1 μm/minute and the porous layer, 20 μm in thickness, was obtained in about 20 minutes.

[Fig. 2B] On the porous Si layer 202 mentioned above, a single crystal Si layer 203 was epitaxially grown to a thickness of 0.25 μm by the CVD method. The conditions for the deposition of this layer were as

follows.

Kind of gas used: SiH_4/H_2

Flow volume of gas: 0.62/140 (l/min)

Temperature: 850°C

Pressure: 80 Torrs

Rate of growth: 0.12 μm/min

[Fig. 2C] The substrate 201 manufactured by the method described above was treated in an atmosphere of steam at 900°C to obtain an oxide film 204, 0.1 μm in thickness.

[Fig. 2D] The substrate having formed an oxidized surface as mentioned above was used as the first Si substrate and a 5-inch P type Si substrate (10 Ωcm - 20 Ωcm) prepared in advance was used as the second Si substrate. These two substrates were washed with a system using acid and ammonia, finally washed with a dilute hydrofluoric acid solution (1.5%), rinsed with purified water, spin dried, and pasted together on the obverse surfaces thereof. The pasted substrates were heat-treated at 1100°C for two hours.

[Fig. 2E] After the heat treatment, the Si substrate part 201, about 600 μm in thickness, on the first substrate side was ground with a surface grinder. After the porous Si layer 202 was exposed, the substrate was immersed in a selective etching solution and exposed to an ultrasonic wave until the porous part 202 alone was wholly etched selectively. The

composition of the selective etching solution, the etching speed relative to the single crystal Si layer, and the etching speed relative to SiO_2 were as shown below.

Selective etching solution: Aqueous TMAH solution (24 ppm)

Si etching speed: 5 Å/min

SiO_2 etching speed: Not more than 1 Å/minute

As a result, a SOI substrate provided with a single crystal Si film, about 0.2 μm in thickness, was completed on the SiO_2 layer, 0.1 μm in thickness. Microvoids inevitably occurred in the completed SOI wafer had diameters in the approximate range of 0.5 μm - 3 μm and a density of not more than 0.5 piece/cm^2. The SOI film had a very satisfactory thickness distribution, 0.2 μm ± 1.5%.

A comparative sample produced at the same time, with the washing prior to the pasting discontinued at the step using the NH_4OH : H_2O_2 : H_2O solution (the silicon surface rendered hydrophilic), was on a par with the comparative sample of Example 1 in terms of microvoids but had voids, several mm in diameter, formed in an annular pattern similarly to the comparative example.

Example 4:

Now, the fourth example of this invention will be described in detail below with reference to Figs. 3A to

3D.

First, a 5-inch single crystal P type Si substrate (0.01 Ωcm - 0.02 Ωcm) 301 having a thickness of 625 μm was prepared, set in place in such an apparatus as illustrated in Fig. 4A, and subjected to anodic formation to have the surface of the Si substrate 301 converted into a porous Si layer 202 in a thickness of 20 μm. For the anodic formation, a 49% HF solution was used as the solution 304 and the current density was set at 0.8 mA/cm^2. The formation of the porous texture proceeded at a rate of about 0.8 μm/minute and the porous layer, 20 μm in thickness, was obtained in about 25 minutes.

[Fig. 3B] On the porous Si layer 302 mentioned above, a single crystal Si layer 303 was epitaxially grown to a thickness of 1.5 μm by the CVD method. The conditions for the deposition of this layer were as follows.

Kind of gas used: SiH_2Cl_2/H_2

Flow volume of gas: 0.45/200 (l/min)

Temperature: 950°C

Pressure: 760 Torrs

Rate of growth: 0.25 μm/min

[Fig. 3A] The substrate 301 manufactured by the method described above was used as the second Si substrate (no oxide film formed herein). This second Si substrate and a separately prepared P type Si

substrate (10 Ωcm - 20 Ωcm) 310 were oxidized in an atmosphere of steam at 1050°C to a thickness of 1.5 μm.

[Fig. 3C] These two substrates were washed with a system using acid and ammonia, finally washed with a dilute hydrofluoric acid solution (1.5%), rinsed with purified water, spin dried, and pasted together on the obverse surfaces thereof. The pasted substrates were heat-treated at 1100°C for two hours.

[Fig. 3D] After the heat treatment, the Si substrate part 301, about 600 μm in thickness, on the second substrate side was ground with a surface grinder. After the porous Si layer 302 was exposed, the substrate was immersed in a selective etching solution and exposed to an ultrasonic wave until the porous part 302 alone was wholly etched selectively. The composition of the selective etching solution, the etching speed relative to the single crystal Si layer, and the etching speed relative to SiO_2 were as shown below.

Selective etching solution: Aqueous 0.005% hydrofluoric acid solution

Si etching speed: 3 Å/min

SiO_2 etching speed: 2 Å/min

As a result, a SOI substrate provided with a single crystal Si film, about 1.5 μm in thickness, was completed on the SiO_2 layer, 1.5 μm in thickness.

Microvoids inevitably occurred in the completed SOI wafer had diameters in the approximate range of 0.5 μm - 3 μm and a density of not more than 0.3 piece/cm^2.

A comparative sample produced at the same time, with the washing prior to the pasting discontinued at the step using the NH_4OH : H_2O_2 : H_2O solution (the silicon surface rendered hydrophilic), was on a par with the comparative sample of Example 1 in terms of microvoids but had voids, several mm in diameter, formed in an annular pattern similarly to the comparative example.

What is claimed is:

1. A method of manufacturing an SOI substrate comprising the steps of:

superposing a first substrate (101;201;310) having a silicon oxide surface (102;204;304) and a second substrate (110;210;301) having a silicon surface upon each other so that said silicon oxide surface and said silicon surface contact each other; and

heat treating the superposed substrate, characterised by the step of:

washing said silicon surface of said second substrate (110;210;301) prior to said superpositioning step so said silicon surface acquires hydrophobicity and has a water content of not more than 6×10^{13} molecules/cm^2.

2. A method of manufacturing an SOI substrate according to claim 1, wherein said second substrate comprises a silicon substrate (110;210).

3. A method of manufacturing an SOI substrate according to claim 1 or 2 wherein said first substrate comprises a silicon substrate (101) having a silicon oxide layer (102) formed on a surface.

4. A method of manufacturing an SOI substrate according to any of claims 1-3, further comprising the step of

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reducing the thickness of said first substrate (101) after said first substrate (101) is bonded to said second substrate (110).

5. A method of manufacturing an SOI substrate according to any of claims 1-3, further comprising the step of reducing the thickness of said second substrate (110) after said first substrate (101) is bonded to said second substrate (110).

6. A method of manufacturing an SOI substrate according to claim 4 or 5 wherein said reducing step comprises reduces the thickness of a substrate by polishing.

7. A method of manufacturing an SOI substrate according to claim 4 or 5 wherein said reducing step comprises reducing the thickness of a substrate by etching.

8. A method of manufacturing an SOI substrate according to claim 1, wherein said first substrate comprises a porous silicon layer (202), a single crystal silicon layer (203) and a silicon oxide layer (204), successively laminated on a silicon substrate (201).

9. A method of manufacturing an SOI substrate according to claim 8 wherein said second substrate comprises a silicon substrate (210).

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10. A method of manufacturing an SOI substrate according to claim 8 or 9 further comprising the step of removing said silicon substrate (201) and said porous silicon layer (202) after said single crystal silicon layer (203) is bonded to said second substrate (210).

11. A method of manufacturing an SOI substrate according to claim 10, wherein said silicon oxide substrate (201) is removed by grinding.

12. A method of manufacturing an SOI substrate according to claim 10 wherein said silicon substrate (201) is removed by etching with an alkaline solution.

13. A method of manufacturing an SOI substrate according to any of claims 10-12 wherein said porous silicon layer (202) is removed by etching with a solution containing hydrofluoric acid or with an alkaline solution.

14. A method of manufacturing an SOI substrate according to claim 1 wherein said first substrate comprises a silicon substrate (310) having a silicon oxide layer (304) formed on a surface.

15. A method of manufacturing an SOI substrate according to claim 14 wherein said second substrate comprises a porous silicon layer (302) and a single crystal silicon

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layer (303) successively laminated on a silicon substrate (301).

16. A method of manufacturing an SOI substrate according to claim 15 further comprising the step of removing said silicon substrate (301) and said porous silicon layer (302) from said single crystal silicon layer (303) after said single crystal silicon layer is bonded to said silicon oxide layer (304) of said first substrate.

17. A method of manufacturing an SOI substrate according to any preceding claim wherein the silicon surface of said second substrate (110;210;301) is washed with a solution containing hydrofluoric acid.

18. A method of manufacturing a SOI substrate according to claim 17 wherein said washing solution comprises hydrofluoric acid at a concentration of 1.5%.

19. A method of manufacturing an SOI substrate in accordance with any preceding claim wherein said heat treating step comprises heating said superposed substrate to a temperature of between 900° to 1100°C.

20. A method of manufacturing a SOI substrate according to claim 17, wherein after washing said silicon surface with said solution containing hydrofluoric acid and then rinsing the resultant surface with pure water, the rinsed resultant is dried; and wherein said heat-treatment is carried out at 900°C or more.

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21. A method of manufacturing an SOI substrate according to any of the preceding claims, wherein said heat-treating after the superposing step is carried out in an oxidizing atmosphere.

22. A method of manufacturing an SOI substrate according to any of the preceding claims, wherein a same washing as conducted to said second substrate is conducted to said first substrate.

23. An SOI substrate produced by a method according to any of the preceding claims.

