26 JUN 2002

G00002

METHOD AND APPARATUS FOR HEAT-TREATING AN SOI SUBSTRATE AND METHOD OF PREPARING AN SOI SUBSTRATE BY USING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a method and an apparatus for heat-treating an SOI substrate and also to a method of preparing an SOI substrate by using the same. More particularly, the present invention relates to a method and an apparatus for heat-treating an SOI subsrate having a silicon film, and also to a method of preparing an SOI substrate by using the same.

Related Background Art

In the technological field of silicon type semiconductor devices and integrated circuits, a large number of researches have been made to date on devices having a semiconductor on insulator (SOI) structure produced by utilizing a single crystal semiconductor film formed on a film insulator because such devices provide a reduced parasitic capacitance, an improved resistance against radiation and an easy device isolation, which can lead to a high speed/low voltage operation of transistors, a low power consumption rate, an enhanced degree of adaptability to integration and a significant reduction in the number of manufacturing steps including elimination of the well-producing

166166

26 JUN 2002

steps.

Known substrates having an SOI structure (SOI substrates) include SOS (silicon on sapphire) substrates, those prepared by oxidizing the surface of an Si single crystal substrate, forming a window to expose part of the Si substrate and realizing a lateral epitaxial growth by using that area as seed to form a Si single crystal film (layer) on the SiO_2 surface, those prepared by using a Si single crystal substrate itself as active layer and forming a silicon oxide film thereunder, those prepared by using a substrate having a dielectrically isolated Si single crystal region on a thick poly-crystalline Si layer and surrounded by a V-shaped groove and SOI substrates prepared by means of dielectric isolation involving oxidation of porous Si, which is referred to as FIPOS (full isolation by porous silicon).

Recently, the SIMOX (separation by implanted oxygen) technology and the wafer bonding technology seem to be in the main stream of the technological field of producing SOI structures. The SIMOX technology was reported for the first time in 1978 (K. Izumi, M. Doken and H. Ariyoshi, Electron. Lett. 14 (1978) p.593). It provides a method of forming a buried silicon oxide film by implanting oxygen ions into a silicon substrate and subsequently heat-treating it at high temperature.

26 JUN 2002

The wafer bonding technology provides, on the other hand, a variety of techniques for thinning one of the bonded wafers in the process of producing an SOI structure.

(BPSOI)

This is one of the most basic processes that utilizes polishing. A silicon oxide film is formed on the surface of one or both of a pair of wafers, which are bonded together. Subsequently, one of the wafers is thinned by grinding and polishing.

(PACE)

The plasma assisted chemical etching (PACE) process was developed to improve the uniformity of film thickness of an SOI layer obtained by polishing. With this technique, the film thickness is measured at thousands of highly densely distributed measuring points on the wafer. Then, a plasma source having a diameter of several millimeters is driven to scan the film at a scanning rate corresponding to the film thickness to vary the etching rate as a function of the film thickness distribution and thereby reduce the variations in the film thickness.

(Cleave Process using Hydrogen Ion Implantation)

A novel technique for producing a bonded SOI substrate was recently reported by M. Bruel in Electronics Letters, 31 (1995) p.1201 and also disclosed in Japanese Patent Application Laid-Open No.

26 JUN 2002

5-211128 and U.S. Patent No. 5,374,564. With this process, an oxidized wafer that has been implanted with ions of a light element such as hydrogen or an inert gas element over the entire surface thereof is bonded to another wafer and subsequently heat-treated. Then, the wafer is cleaved during the heat treatment at the depth to which ions have been implanted. As a result, the layer located above the projection range of implanted ions is transferred onto the other wafer to produce an SOI structure.

(Epitaxial Layer Transfer)

Japanese Patent No. 2608351 and U.S. Patent No. 5,371,037 describe an excellent technique for preparing an SOI substrate by transferring a single crystal layer on a porous layer onto another substrate. This technique is also referred to as "ELTRAN (registered tradename)" (T. Yonehara, K. Sakakguchi, N. Sato, Appl. Phys. Lett. 64 (1994), p.2108).

As discussed above, in the field of SOI substrates, smoothing the rough surface produced as a result of etching, ion implantation and subsequent heat treatment and forming an SOI layer of silicon film with a low boron concentration by partly removing boron atoms diffused into the single crystal layer are the major problems that have to be solved somehow to improve the withstand voltage of the gate oxide film and the carrier mobility of MOSFET in order to improve

26 JUN 2002

the performance of silicon type semiconductor devices. Thus, various techniques have been proposed to solve these problems for each of the above listed methods for preparing SOI substrates.

With the cleave process using hydrogen ion implantation, the surface of the wafer separated along the ion projection range shows a root-mean-square of surface roughness (Rrms) of 10nm and the surface layer has damages caused by ion implantation. Such a wafer is smoothed to remove the layer damaged by ion implantation by polishing and removing the surface layer to a small extent, using a technique referred to as "touch polishing" (M. Bruel, et al., Proc. 1995 IEEE Int. SOI Conf. (1995) p.178).

In the case of the PACE technique, the surface roughness up to 10.66nm (as peak-to-valley value) is detected by means of an atomic force microscope immediately after the plasma etching process. Such rough surface is then smoothed to 0.62nm, or the level equivalent to the original surface roughness, by touch polishing for removing the surface only to a slight extent (T. Feng, M. Matloubian, G. J. Gardopee, and D. P. Mathur, Proc. 1994 IEEE Int. SOI Conf. (1994) p.77).

When the BESOI technique is used, the surface roughness of about 5 to 7nm peak to valley produced at the end of the etching process is removed only by removing the surface layer by three to five times of

the surface roughness or by 20 to 30nm. As a result of this polishing process, the uniformity of film thickness is degraded by 0.005μm (=5nm) in average.

Thus, when touch polish or kiss polish, as it is often called, is used to polish the surface only to a slight extent, the surface roughness may be removed but, at the same time, the film thickness will be reduced to consequently degrade the uniformity of film thickness. While the polishing operation is terminated generally by controlling the duration of the operation, it is a known fact that, if the polishing time is constant, the extent of polishing varies within the same surface of a wafer, among the surfaces of different wafers and from batch to batch depending on the polishing solution, the temperature of the surface table during the polishing operation and how much the emery cloth is worn and hence it is very difficult to keep the extent of polishing to a constant level. Particularly, it is known that the wafer is normally polished more along the outer periphery.

Additionally, it is impossible to reduce the boron concentration if boron is diffused across the entire depth of the SOI layer to show a high concentration level. The surface roughness of the SOI layer of a wafer prepared by the SIMOX technique using oxygen ion implantation is greater than that of the bulk normally by a digit. S. Nakashima and K. Izumi (J. Mater. Res.

(1990) Vol. 5, No. 9, p.1918) reported that the surface roughness with innumerable recesses having a diameter of tens of several nanometers can be eliminated by heat-treating the surface at 1260°C (in a nitrogen atmosphere) for 2 hours or at 1300°C (in an argon atmosphere containing oxygen by 0.5%) for 4 hours. They also reported that the surface roughness will not change by a heat treatment at 1150°C. However, it is practically impossible to use a quartz tube for a heat treatment conducted at temperature higher than 1200°C in terms of thermal resistance. Additionally, a process using such high temperature makes the introducing of slip lines serious as the wafer size inreases.

With the oxygen implantation technique, there may arise a problem that boron atoms contained in the clean room adhere to the surface of the substrate and implanted into the wafer in the operation of implanting oxygen ions (Co-implantation) and the boron atoms that have adhered to the wafer before the high temperature heat treatment process for turning the oxygen contained in the wafer by ion implantation into a silicon oxide layer can be diffused into the entire silicon layer by the heat treatment. A similar problem may be produced in a bonded SOI substrate by boron atoms contained in the clean room.

The inventors of the present invention proposed in

Japanese Patent Applications Laid-Open Nos. 5-218053 and 5-217821 a technique for smoothing the surface of an SOI substrate by heat-treating it in a hydrogen-containing atmosphere.

The surface of an SOI substrate that may carry undulations after the etching process and hence is rougher than the polished surface of a commercially available silicon wafer can be smoothed by hydrogen annealing to a level of smoothness comparable to the polished surface of such a commercially available silicon wafer. At the same time, the boron concentration of the single crystal silicon film can be reduced by annealing the substrate having a single crystal silicon film formed on an insulator in a hydrogen atmosphere and externally diffusing boron into the gas phase. While the rate of diffusion of boron is relatively high in silicon, it is low in a naturally oxidized silicon oxide layer that is typically formed on the surface of the substrate during a heat treatment process conducted in an oxygen or inert gas atmosphere so that boron will remain and be confined within the silicon layer. However, the silicon oxide film formed on the surface of the SOI layer and operating as diffusion barrier can be removed and any possible subsequent formation of oxide film during the process can be effectively suppressed by annealing the substrate in a reducing atmosphere typically containing

26 JUN 2002

hydrogen so that, as a result, the external diffusion of boron is encouraged and, if boron is contained in the entire SOI layer to a high concentration level, the impurity concentration of the entire SOI layer can be reduced to a level that is feasible for device fabrication by that external diffusion of boron (N. Sato and T. Yonehara, Appl. Phys. Lett. 65 (1994) p.1924).

Thus, a heat treatment in a hydrogen-containing atmosphere is a highly effective way for externally diffusing boron contained in the silicon layer and smoothing the surface thereof showing a remarkable degree of roughness.

A heat treatment in a hydrogen-containing atmosphere is also highly effective for preparing an SOI substrate by means of the SIMOX technique. The above paper also reports that the surface roughness can be smoothed satisfactorily by heat treatment conducted at or below 1200°C in a hydrogen-containing atmosphere.

When annealing an SOI substrate by means of hydrogen, the rate of reduction of the film thickness will be 0.08nm/min. at 1150°C, which is much lower than the rate of reduction by polishing. However, when annealing a bulk wafer in place of an SOI substrate by emans of hydrogen, a relatively high rate of reduction of 10 to 100nm/min. in the film thickness is reported by in B. M. Gallois et al., J. Am. Ceram. Soc., 77

26 JUN 2002

(1994) pp.2949. It will be appreciated that the uniformity of film thickness is apt to be degraded in a same wafer surface and among the surfaces of different wafers when the rate of film thickness reduction and the etching rate are not controlled properly.

Thus, it is highly important to precisely control the film thickness for each wafer and among different wafers because noticeable variations in the film thickness of the SOI layer can significantly affect the performance of the devices produced as final products particularly in terms of the characteristics including the threshold voltage of SOI-MOS transistor of fully depleted type.

There are requirements to be met by an SOI substrate other than the uniformity of film thickness.

The film thickness of the SOI layer varies depending on the characteristics of the semiconductor device to be produced by using the SOI substrate. From the viewpoint of designing SOI substrates, it is preferred that the film thickness of the SOI layer of the SOI substrate does not fluctuate by heat treatment.

SUMMARY OF THE INVENTION

Thus, it is an object of the present invention to provide a method and an apparatus for heat-treating an SOI substrate adapted to suppressing with ease the etching and always uniformly smoothing the surfaces of

26 JUN 2002

a plurality of substrates, as well as a method of preparing an SOI substrate by using such a method and such an apparatus.

Another object of the present invention is to provide a method and an apparatus for heat-treating an SOI substrate adapted to efficiently reducing impurities such as boron contained in the film, while maintaining the uniformity of film thickness, as well as a method of preparing an SOI substrate by using such a method and such an apparatus.

Still another object of the present invention is to provide a method and an apparatus for heat-treat an SOI substrate adapted to reducing the variations in the performance among the devices produced by using the SOI substrate, as well as to a method of preparing an SOI substrate by using such a method and such an apparatus.

A further object of the present invention is to provide a method and an apparatus for heat-treating an SOI substrate at low cost adapted to obtaining a desired film thickness and a surface condition substantially free from surface defects, as well as to a method of preparing an SOI substrate by using such a method and such an apparatus.

According to an aspect of the present invention, there is provided a method for heat-treating an SOI substrate having a silicon surface comprising a step of:

26 JUN 2002

heat-treating the SOI substrate in a hydrogen-containing reducing atmosphere, with keeping the SOI substrate in a state disposed opposite to a plane comprising a material comprised of a non-oxidized silicon as a main component with a predetermined distance separating them.

According to another aspect of the present invention, there is provided an etching apparatus for carrying out the heat treatment method.

According to still another aspect of the present invention, there is provided which comprises a reaction furnace having an inner surface comprising non-oxidized silicon and adapted to contain an SOI substrate and reduce the internal pressure.

According to a further aspect of the present invetion, there is provided a method of preparing an SOI substrate, which comprises a steps of:

smoothing a surface of the SOI substrate by the heat treatment method in above.

According to a further aspect of the present invention, there is provided a method of preparing an SOI substrate having a silicon film, which comprises steps of:

bonding a second article and a first article containing a separation layer for defining a separating position;

transferring the silicon film onto the second

26 JUN 2002

article by separating the bonded first and second articles at the layer defining the separating position;

arranging a plane surface of non-silicon oxide opposite to the silicon film transferred onto the second article and heat-treating the silicon film in a hydrogen-containing reducing atmosphere.

According to a further aspect of the present invention, there is provided a method of preparing an SOI substrate having a silicon film, which comprises steps of:

bonding a first article and a second article;

removing a part of the first article from the bonded first and second articles so as to leave a silicon film on the second article; arranging a plane non-oxidized silicon surface opposite to an unpolished surface of the silicon film; and heat-treating the silicon film in a hydrogen-containing reducing atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross sectional view of an embodiment of heat treatment apparatus according to the invention.

FIG. 2 is a graph showing the dependency of the etching rate on the material of the counter-surface.

FIG. 3 is a graph showing the etching rate when

26 JUN 2002

the materials of the oppositely disposed surfaces are Si and SiO_2.

FIG. 4 is a graph showing the rate of removing Si atoms when the materials of the oppositely disposed surfaces are Si and SiO_2.

FIG. 5 is a schematic cross sectional view of another embodiment of heat treatment apparatus according to the invention.

FIG. 6 is a schematic cross sectional view of a still another embodiment of heat treatment apparatus according to the invention, showing a principal area thereof.

FIG. 7 is a schematic cross sectional view of a pair of counter-surface constituting members, showing a mode of arrangement that can be used for the purpose of the invention.

FIG. 8 is a schematic cross sectional view of a semiconductor article and a counter-surface constituting member, showing another mode of arrangement that can be used for the purpose of the invention.

FIG. 9 is a schematic cross sectional view of a still another embodiment of heat treatment apparatus according to the invention, showing a principal area thereof.

FIG. 10 is a schematic cross sectional view of still another embodiment of heat treatment apparatus

FIG. 11 is a flow chart for a mode of carrying out a method of preparing a semiconductor article by using a heat treatment method according to the invention.

FIG. 12 is a flow chart for another mode of carrying out a method of preparing a semiconductor article by using an etching method according to the invention.

FIGS. 13A, 13B, 13C and 13D are schematic illustrations of a method of preparing a semiconductor article by using a heat treatment method according to the invention and a cleave process by ion implantation.

FIGS. 14A, 14B, 14C, 14D and 14F are schematic illustrations of a method of preparing a semiconductor article by using a heat treatment method according to the invention and an epitaxial layer transfer process.

FIG. 15 is a schematic illustration of a heat treatment method according to the invention, showing its smoothing effect.

FIGS. 16A, 16B, 16C and 16D are schematic illustrations showing how articles are arranged for a heat treatment operation for the purpose of the invention.

FIG. 17 is a graph illustrating the location dependency of the film thickness reduction in the furnace in a heat treatment process according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 is a schematic cross sectional view of an embodiment of heat treatment apparatus according to the invention.

This heat treatment apparatus comprises a reaction furnace 1 operating as heat treatment chamber and adapted to contain a semiconductor article (SOI substrate) W and get evacuated and a heater 2 for heating the article W and the gas contained in the furnace 1. It is connected to a hydrogen gas source 5 by way of at least a valve 6 and also to an exhaust pump 8 by way of at least a valve 7.

A counter-surface constituting member 3 that has a plane surface of a material containing non-oxidized silicon 4 as principal ingredient is arranged at the side of the surface of the article W to be treated with a predetermined gap AS interposed therebetween. In FIG. 1, numeral 9 denotes a support member for supporting both the article W and the counter-surface constituting member 3.

The heat treatment operation using this embodiment proceeds in a manner as described below.

Firstly, an article W and an counter-surface constituting member 3 are placed in the reaction furnace 1 with a predetermined gap AS interposed therebetween and the inside of the furnace is evacuated by the exhaust pump 8 to reduce the internal pressure.

26 JUN 2002

Then, they are heated by the heater 2.

Thereafter, hydrogen gas is introduced into the furnace from the gas source 5. The inside of the furnace and the article W are held to a predetermined temperature level by controlling the heat generation of the heater 2.

Then, as a result, silicon is annealed from the surface (to be treated) of the article W.

The article (SOI substrate) W to be heat-treated by a method according to the invention may be an SOI wafer of any of the above described types prepared by using a bulk Si wafer prepared by means of a CZ process, an epitaxial Si wafer having an epitaxially grown layer or an Si wafer obtained by treating a bulk Si wafer by means of a hydrogen annealing process or a vitreous silica substrate having a silicon film. In particular, it is preferably an SOI wafer that has been subjected to a surface treatment process after polished and is carrying undulations on the surface, an SOI wafer having an unpolished surface or an SOI wafer on the way of preparation using a bonding process or a SIMOX process.

Since an article W is heat-treated in an hydrogen-containing atmosphere according to the invention, the source gas to be fed into the furnace refers to 100% hydrogen gas, inert gas such as inert gas containing hydrogen by 1 to 99%. Preferably,

26 JUN 2002

relatively highly pure hydrogen gas that is sufficiently free from moisture is fed into the furnace by way of a hydrogen refining system (hydrogen purifier) so that the reducing atmosphere may show a dew point not higher than -92°C.

The oxygen and moisture content of the atmosphere should be held to a minimal level because any oxygen and moisture remaining in the atmosphere can oxidize silicon on the surface of the article W to produce a film coat as the temperature is raised and the produced film coat by turn obstructs the process of smoothing the surface and also because the residual oxygen and moisture can give rise to an unexpected reduction in the silicon film thickness as a side effect of oxidation and etching. This is why it is desirably to control the atmosphere so as to make it show a dew point not higher than -92°C.

While the hydrogen-containing atmosphere may show a pressure level higher than, equal to or lower than the atmospheric pressure, its pressure is preferably equal to or lower than the atmospheric pressure, although a lower pressure level may be advantageous to improve the surface smoothing effect and the effect of externally diffusing the impurities. When an etching furnace is made from fused quartz, the lower limit of the pressure of the atmosphere in the furnace is preferably set to 3.9×10^4Pa, more preferably to 6.6×10^4

26 JUN 2002

Pa in order to prevent the furnace from being deformed.

In view of the above considerations, it is reasonable to select a pressure level between the atmospheric pressure and 1.3Pa for the pressure of the atmosphere in the furnace, taking the operation environment into consideration.

Although there is no limit for the flow rate of hydrogen-containing gas to be used for the purpose of the invention, the flow rate as discussed below is preferably used.

The flow rate as used herein refers to the flow rate of gas passing through an area obtained by subtracting the cross sectional area of the semiconductor article from the cross sectional area of the furnace tube. If the gas flow rate is too high, the rate of removing the reaction product from the surface of the article is raised to reduce the etching suppressing effect.

If, on the other hand, the gas flow rate is too low, the rate of removing the reaction product from the surface of the articles is remarkably reduced to reduce the effect of removing the impurities such as boron by externally diffusing them from the semiconductor single crystal layer.

For the purpose of the invention, the gas flow rate is preferably 10 to 300cc/min•cm^2, more preferably 30 to 150cc/min•cm^2. The gas flow rate is a parameter

26 JUN 2002

for controlling the rate of diffusing and removing the reaction product from the surface to the lateral sides of the article.

The surface of the article is satisfactorily etched and smoothed in a hydrogen-containing atmosphere at temperature below 1,200°C, at which the surface may not be smoothed in a nitrogen atmosphere or a inert gas atmosphere. For the purpose of the invention, the temperature to be used for the etching process that has a smoothing effect depends on the composition and the pressure of gas. More specifically, the temperature is found within a range whose lower limit is preferably not lower than 300°C, more preferably not lower than 500°C, further preferably not lower than 800°C. On the other hand, the upper limit of the temperature range is preferably not higher than the melting point of silicon, more preferably not higher than 1,200°C. If the smoothing process proceeds too slowly, a smoothed surface can be obtained by using a longer period of time for the heat treatment.

For the purpose of the invention, while the counter-surface constituting member 3 may be made of any material so long as the counter-surface carries a material containing non-oxidized silicon as principal ingredient, it is preferably an Si wafer from which any natural oxide film is removed, an Si wafer having a film of non-oxidized silicon such as silicon nitride or

26 JUN 2002

silicon carbide on the surface or vitreous quartz wafer having a surface on which a film of non-oxidized silicon such as Si, SiN or SiC is formed. A wafer having a structure same as the article to be heat-treated may preferably be used for the counter-surface constituting member 3 if the counter-surface carries silicon oxide film thereon.

The counter-surface should be plane and held in parallel with the surface to be treated. As for size and shape, the counter-surface preferably has a size equal to or greater than that of the surface to be treated of the article W and a profile similar to that of the article W.

The counter-surface constituting member 3 may preferably be part of the support member 9, which may typically be a tray. While the distance, or the gap AS, separating the counter-surface and the article may vary as a function of the silicon surface area (to be annealed) of the semiconductor article, it is preferably not greater than 20mm, more preferably not greater than 10mm, to achieve an effect of suppressing the etching due to the interaction of the oppositely disposed surfaces, when the semiconductor article has a diameter greater than 100mm. Although the distance between the oppositely disposed surfaces has no lower limit, it is preferably not smaller than 1mm, more preferably not smaller 3mm.

26 JUN 2002

A surface smoothing process starts when the cleansed surface of the semiconductor article W is heat-treated. Therefore, if the surface of the article is coated with a thick natural oxide film, it is preferably removed by etching, using dilute hydrofluoric acid in order to make the surface smoothing process start early.

The silicon surface smoothed in this way is highly suited for preparing semiconductor devices.

Thus, according to the invention, a thin SOI layer having a thickness less than 450nm or a particularly thin and uniform SOI layer having a thickness between 20nm and 250nm can be produced without difficulty.

Then, the obtained surface is smoothed and will show, for example, an Rrms value of at least not greater than 0.4nm, preferably not greater than 0.2nm, more preferably not greater than 0.15nm, in a 1μm square area.

Hydrogen containing gas may be introduced into the furnace in any appropriate manner as will be described hereinafter and the present invention is not limited to the arrangement of FIG. 1 in terms of the way of introducing gas into the furnace.

As for the material of the reaction furnace 1, the reaction furnace is preferably made of a material consisting of non-oxidized silicon particularly for the inner surface of an area located close to the article

26 JUN 2002

W. For example, the use of an SiC reaction tube is preferable.

For the purpose of the invention, the heater 2 may be a resistance heater, a high frequency heater or a lamp.

Now, some of the findings that have led to the present invention will be described below.

(Findings on the Dependency of the Etching Rate on the Material of the Counter-Surface)

The inventors of the present invention looked into the conditions for the heat treatment to be conducted in a hydrogen-containing atmosphere in order to remove fine undulations on a silicon single crystal surface and found that the rate of etching single crystal silicon varies remarkably depending on the material of the surface opposing the single crystal silicon surface (counter-surface). FIG. 2 is a graph showing the dependency of the etching rate on the material of the counter-surface and the heat treatment temperature. In the graph of FIG. 2, the lower horizontal axis represents the reciprocal number of temperature (T) and the upper horizontal axis represents the temperature corresponding to 1/T, whereas the vertical axis represents the logarithmically expressed etching rate (nm/min.). The film thickness of the SOI layer or the single crystal silicon layer on a buried insulator can be observed without difficulty by means of a

26 JUN 2002

commercially available light-reflection type film thickness gauge. Then, the etching rate can be determined by observing the film thickness before and after the heat treatment with varied durations and calculating the change with time of the film thickness.

In FIG. 2, data set A represents the etching rate that varies as a function of temperature when an counter-surface of Si is arranged opposite to an article of SiO_2 that is etched. The activation energy Ea as obtained from the inclination of the approximate line produced by using the method of least squares of the observed values on the plot was about 4.3eV.

Data set B in FIG. 2 represents the etching rate in a heat treatment process when a counter-surface of SiO_2 is arranged opposite to an article of Si that is etched. Data set C in FIG. 2 represents the etching rate in another heat treatment process when a counter-surface of Si is arranged opposite to an article of Si that is etched. The activation energy Ea of this heat treatment was about 4.1eV.

Finally, data set D in FIG. 2 represents the etching rate in another heat treatment process when a counter-surface of SiO_2 is arranged opposite to an article of SiO_2 that is etched. The activation energy Ea of this heat treatment was about 5.9eV.

As seen from data sets B and C FIG. 2, with a heat treatment conducted in a hydrogen-containing

26 JUN 2002

atmosphere, the silicon etching rate is increased by 9 times without changing the temperature when the counter-surface of silicon is replaced by a counter-surface of silicon oxide.

More specifically, the etching rate is as low as about 0.045nm/min. at 1,200°C when two single crystal silicon surfaces are arranged vis-a-vis, or a silicon counter-surface is arranged opposite to a silicon surface to be etched (C in FIG. 2). Only less than 3nm of the film is etched out after 60 minutes in the heat treatment. To the contrary, the etching rate is raised to about 0.36nm/min. at 1,200°C so that as much as 21.6nm of the film is etched out after an hour when a silicon oxide counter-surface is arranged opposite to a silicon surface to be etched (D in FIG. 2). This etching thickness is comparable with that of a touch polish process.

FIG. 3 is a graph showing the etching rate when the materials of the oppositely disposed surfaces are Si and SiO_2. In FIG. 3, the horizontal axis represents the etching time (min.) whereas the vertical axis represents the etching thickness (nm) and the heat treatment is conducted at temperature T of 1,200°C. In FIG. 3, the white circles show the values obtained when the article has an SiO_2 surface and the counter-surface is made of Si, whereas the black circles show the values observed when the article has an Si surface and

the counter-surface is made of SiO_2.

As seen from FIG. 3, with a same duration of heat treatment, film is etched out to a greater extent when the article has an SiO_2 surface and the counter-surface is made of Si as indicated by white circles than when the article has an Si surface and the counter-surface is made of SiO_2 as indicated by black circles. In short, when an SiO_2 surface and an Si surface are oppositely arranged for heat treatment, the SiO_2 surface is etched to a greater extent than the Si surface.

FIG. 4 is a graph showing the rate of removing Si atoms when an SiO_2 surface is etched, using an Si counter-surface, and that of removing Si atoms when an Si surface is etched, using an SiO_2 counter-surface is used, as obtained by calculation on the basis of FIG. 3. In FIG. 4, the horizontal axis represents the etching time and the vertical axis represents the number of removed Si atoms (atmos/cm^2), the observed SiO_2 surfaces being indicated by white circles, triangles and squares, the observed Si surfaces being indicated by black circles, triangles and squares.

It will be appreciated from FIG. 4, which shows the number of removed silicon atoms calculated from the etched volume of a silicon oxide surface and also the number of silicon atoms calculated from the etched volume of a single crystal silicon surface as illustrated in FIG. 3, that the number of removed

silicon atoms is substantially same for the two surfaces, meaning that, when an Si surface and an SiO_2 surface are arranged oppositely relative to each other for heat treatment, Si atoms will be lost substantially at a same rate from the two surfaces.

Thus, the rate of etching a silicon surface is accelerated by the interaction with a silicon oxide surface arranged opposite to it. This interaction will generally be expressed by the reaction formula shown below, where silicon and silicon oxide react with a ratio of 1:1.

$$Si + SiO_2 \rightarrow 2SiO$$

The Si etching rate is affected by the distance between the Si surface and the counter-surface. It has been found that, when a silicon counter-surface is used, the etching rate is reduced as the distance separating the two surfaces is reduced. When, on the other hand, a silicon oxide counter-surface is used, the etching rate is raised as the distance between the two surfaces is reduced.

Additionally, the etching rate is remarkably low when the etching process is conducted in an atmosphere containing no reducing gas, which is typically hydrogen gas, if compared with the etching rate observed when the atmosphere contains reducing gas. In short, the presence of reducing gas, which is typically hydrogen gas, can significantly accelerate the etching rate.

When a silicon surface and a silicon oxide surface are arranged opposite to each other in the etching system, the two surfaces are etched as the material of either one of the surfaces gets to the other one by way of the reaction with the reducing gas, which is typically hydrogen gas. For instance, there may be reactions expressed by $Si+H_2 \rightarrow SiH_2+SiO_2 \rightarrow 2SiO+H_2$. The Si atoms that have left the Si surface are, at least partly, transported through the gas phase to the silicon oxide surface, where they react with SiO_2 to produce SiO, which shows high saturated vapor pressure. Since SiH_2 is consumed as it is needed, the etching process on the Si surface will be promoted. When, on the other hand, two Si surfaces are arranged opposite to each other, the rate of chemical reaction of the Si atoms that have left the Si surfaces proceeds only as a function of the diffusion in the vapor phase once they get to show a saturated concentration level, which hardly becomes high, so that the etching rate will not become very high.

To the contrary, when an Si surface and an SiO_2 surface are opposed, the Si atoms that have left the Si surface are, at least partly, consumed on the surface of the oxide film so that the chemical reaction can proceed without any restrictions. Since SiO that can be produced on the SiO_2 surface shows a high vapor pressure, the reaction can proceed without

26 JUN 2002

restrictions.

When a silicon carbide surface is arranged opposite to a single crystal silicon film, the rate of etching the single crystal silicon film is substantially same as the limited etching rate that is observed when silicon is used for the counter-surface. Likewise, when a silicon nitride surface is arranged opposite to a single crystal silicon film, the rate of etching the single crystal silicon film is also low and substantially same as the limited etching rate observed when silicon is used for the counter-surface.

In short, in a process of heat-treating Si in a hydrogen-containing reducing atmosphere, a material containing silicon and either carbon or nitrogen as principal ingredients or, in other words, a material not containing oxygen as principal ingredient is used for the opposite surface. That is, by using for the counter-surface a material constituted of silicon and a substance that does not react in the above described atmosphere, the etching rate can be reduced to at least less than 1/10, practically equal to 0, if compared with a case where silicon oxide is used for the counter-surface.

(Heat Treatment Apparatus)

While FIG. 1 shows a typical heat treatment apparatus according to the invention, it may be modified in various different ways as will be described

hereinafter.

FIG. 5 is a schematic cross sectional view of another embodiment of heat treatment apparatus according to the invention.

The embodiment of FIG. 5 is so configured that part of hydrogen-containing gas from the gas source 5 is made to pass the gap, or the acting space AS, between the article W and the counter-surface constituting member 3 before it flows into the exhaust pump 8. The exhaust pump 8 is not required in the case of treatment under high pressure or atmospheric pressure.

The mode of arrangement of the article W and the counter-surface constituting member 3 is not limited to the one as shown in FIG. 1, where the they are arranged longitudinally (transversally in the drawing) in parallel with the furnace tube of the furnace 1. They may alternatively be arranged as shown in FIG. 5 or still alternatively be arranged in an inclined fashion or vertically in a horizontal furnace.

Still alternatively, a plurality of articles W may be arranged at intervals and in parallel with each other in a single furnace.

FIG. 6 is a schematic cross sectional view of an embodiment of heat treatment apparatus according to the invention and adapted to collectively heat-treat a plurality of articles.

26 JUN 2002

With the embodiment of etching apparatus of FIG. 6, a plurality of articles, W1, W consisting of an non-oxidized silicon film on the rear surface are arranged in the furnace in such a way that all the front surfaces of the articles are directed upward. Then, since no counter-surface is found for the top article W1, the silicon surface of the article W1 will not be heat-treated in an intended manner. Differently stated, the top article W1 operates as a dummy article. All the articles W except the top article W have a counter-surface located vis-a-vis, which is the non-oxidized silicon rear surface of the directly upper articles W, so that all the silicon surfaces of the articles W will practically not be etched and simply annealed.

When all the articles W1, W are arranged with the silicon front surfaces directed downward, the bottom article operates as a dummy article.

FIG. 6 shows only a principal area of a vertical furnace. When a horizontal furnace having a configuration that can be realized by substantially turning the furnace of FIG. 6 to a lateral side is used, a plurality of articles will be arranged side by side and collectively annealed in a similar fashion.

Note, however, that the furnace of FIG. 6 is adapted only to collectively anneal articles having a non-oxidized silicon rear surface.

26 JUN 2002

FIG. 7 shows an arrangement adapted to heat-treating articles having an oxidized silicon rear surface such as SOI wafers or vitreous silica substrates whose rear surface covered by oxidized silicon.

With this arrangement, a counter-surface constituting member 31 having at least a non-oxidized silicon rear surface is interposed between two adjacent articles so that the Si surface of the lower article W2 is located vis-a-vis the non-oxidized silicon rear surface (counter-surface 4) of the counter-surface constituting member 31. Thus, the Si surface of the article W2 will not be etched but annealed properly. While the counter-surface constituting members 31 of FIG. 7 have a tray-like profile, they are not limited to such a shape and may be replaced by plate-shaped members. Such a member can be prepared by using SiC or Si. Alternatively, it may be prepared by coating the surface of a vitreous silica base with Si, SiC or SiN.

In any case, the distance between the Si surface and the counter-surface is preferably not greater than 20mm, more preferably not greater than 10mm, to achieve an effect of suppressing the etching due to the interaction of the oppositely disposed surfaces, when the semiconductor article has a diameter greater than 100mm.

The rate of etching the silicon on the principal

26 JUN 2002

surface (front surface) of the article during the heat treatment process conducted in a hydrogen-containing atmosphere is accelerated when one or more than one oxidizing impurities such as moisture and/or oxygen are contained in the atmosphere gas. The etching effect due to these gaseous impurities can be reduced by reducing the flow rate of atmosphere gas on and near the principal surface in order to reduce the rate of supply of the impurities such as moisture and/or oxygen. In this manner, the etching process involving the interaction of the silicon surface and the non-oxidized silicon counter-surface can be suppressed. Particularly, the flow rate 12 of atmosphere gas on the front surface of article W can be reduced practically to 0 and the etching potential of the non-oxidized silicon of the counter-surface can be maximally exploited when the article W is so arranged in the furnace tube 1 that the gas flows 11, 14 intersect the direction of the silicon surface of the article and the non-oxidized silicon counter-surface 4 the is located vis-a-vis wafer 81 the silicon surface and separated from the latter by not greater than 20mm as shown in FIG. 8.

Note that, in FIG. 8, there are shown an SOI substrate comprising a buried insulation film 22 and an SOI layer 23 formed on a silicon substrate 21 and a counter-surface constituting member 3 comprising a

26 JUN 2002

silicon substrate from which the natural oxide film, if any, had been removed.

FIG. 9 is a schematic cross sectional view of a heat treatment apparatus prepared by modifying the vertical furnace shown in FIG. 5.

In FIG. 9, a total of four articles W and a dummy article W1 are arranged coaxially and held by respective projections of boat 13, which is the support member of the etching apparatus.

The dummy article W1 is an Si substrate carrying no silicon oxide film on both the front and rear surfaces, whereas the articles W are Si substrates carrying no silicon oxide film on the rear surface.

In this case again, the flow rate of the gas flow 11 passing through the area obtained by subtracting the cross sectional area of the semiconductor articles from the cross sectional area of the furnace tube (outer peripheral area of the furnace tube) is controlled to 10cc/min•cm^2 to 300cc/min•cm^2 and the flow rate of the gas flow 12 on and near the front surface of each article W that is running in parallel with the front surface is made lower than the flow rate of the gas flow 11 running perpendicularly to the front surface in the outer peripheral area of the article W.

Preferably, the flow rate of the gas flow 11 passing through the area obtained by subtracting the cross sectional area of the semiconductor articles from

26 JUN 2002

the cross sectional area of the furnace tube (outer peripheral area of the furnace tube) is controlled to 30cc/min•cm^2 to 150cc/min•cm^2 and the flow rate of the gas flow 12 on and near the front surface of each article W that is running in parallel with the front surface is made practically equal to 0.

FIG. 10 is a schematic cross sectional view of still another embodiment of heat treatment apparatus according to the invention.

This heat treatment apparatus comprises an inner tube 131 having an inner surface of non-oxidized silicon such as SiC, a furnace tube 132 made of fused quartz or vitreous silica and an outer tube 145 having a surface of non-oxidized silicon such as SiC. In FIG. 10, 124, 125 and 145 denote O-rings and 122 and 145 denote flanges, while 126 denotes a sealing closure.

Hydrogen-containing reducing gas is introduced from an inlet port 105 into the space where wafers W are arranged by way of a flow path 141. Then, gas flows further from the opening 135 to the flow path 142 between the furnace tube 132 and the inner tube 131 by way of return-checking means (136, 137) such as non-return valves. Then, gas in the flow path 142 is expelled from the exhaust port 106.

Inert gas such as He, Ar, Ne, N_2, Kr or Xe is introduced into the space 143 between the furnace tube 132 and the hermetically sealed outer tube 145 through

26 JUN 2002

a purge gas inlet port 145 located below and discharged through a purge gas exhaust port 144 located above.

Hydrogen gas would not be brought into contact with silicon oxide heated above 1,000°C until the former is introduced into the space where wafers W are arranged and high temperature prevails. Heat barrier 109 made of foamed quartz, which is silicon oxide, is located outside the high temperature region 150 heated by a heater 2 and, therefore, practically no moisture is generated by hydrogen gas fed through the flow path 141. Therefore, moisture in the supplied hydrogen gas is negligible.

All the components of the apparatus located in the space of the heated high temperature region 150 inside the inner tube 131, where wafers W are arranged, are made of a non-oxidized silicon material such as SiC so that moisture generation is this space is also minimized.

Gas in the inner tube 131 is discharged through an opening 135 located at the center of the tube to produce a uniform gas flow. The furnace tube is a hermetically sealed tube made of silicon oxide such as fused quartz and hence it shows an excellent thermal insulation effect and produces a uniform temperature distribution in the heated high temperature region 150. If hydrogen gas leaks out from the inner tube 131, it would not flow out of the furnace tube 132.

26 JUN 2002

Additionally, the boat 13 for holding wafers W has a surface of non-oxidized silicon such as SiC and hence it would not generate any moisture.

The hermetically sealed outer tube 145 and purge gas prevent metal impurities coming from the heater 2 from entering the inner tube.

The boat 13 has a plane of non-oxidized silicon such as SiC that faces the top wafer W to prevent the top wafer W from being etched.

The rear surface of the wafers W are of non-oxidized silicon as the oxide film, if any, is removed from there to expose silicon or the rear surface is coated with a non-oxidized silicon film.

With any of the above described embodiments of heat treatment apparatus, the furnace 131, the tray 31, the support members 9, 13 preferably are not made of vitreous silica but has a non-oxidized silicon surface typically of SiC, Si or SiN.

The heater 2 may be a resistance heater, a radio frequency heater or a lamp heater. It is preferable that a reaction furnace 1 is provided with a loading chamber having inert gas introducing means and wafers W is transferred from the loading chamber to the reaction furnace 1 while the inside of the furnace 1 is not exposed to gas containing oxygen.

(Method of Preparing an SOI Substrate)

Now, a method of preparing an SOI substrate, using

a heat treatment method according to the invention, will be described.

FIG. 11 is a flow chart for preparing a bonded SOI substrate by means of the cleave process using hydrogen ion implantation or the epitaxial layer transfer process, which may typically be the PACE process.

Firstly a first article is prepared in Step S1. More specifically, hydrogen ions or inert gas ions are implanted into an Si wafer carrying an oxide insulation film formed on at least one of the surfaces to produce a (potential) separation layer at a predetermined depth. Alternatively, the surface of an Si wafer is made porous and the non-porous Si layer is subjected to an epitaxial growth. When the PACE process is used, an Si wafer carrying no oxide film or an Si wafer having its surface oxidized will be prepared.

Meanwhile, a second article is prepared in Step S2. The second article may be an Si wafer obtained by oxidizing the surface of an ordinary Si wafer, an Si wafer having its natural oxide film removed, a vitreous silica wafer or a metal substrate.

Subsequently in Step S3, the first and second articles prepared in Steps S1 and S2 respectively are bonded together directly or indirectly with an adhesive layer interposed therebetween. It will be sufficient when either of the surfaces of the first and second articles to be bonded together carries an insulator

26 JUN 2002

unless an article having a structure other than the SOI structure is prepared.

Before the bonding, the surfaces to be bonded may be activated by irradiating them with ions of hydrogen, oxygen, nitrogen or inert gas.

Then, in Step S4, (unnecessary) part of the first article that has been bonded to the second article (to produce an assembly) is removed. Roughly speaking, two different techniques are available for removing part of the first article. One is the technique of removing part of the first article by grinding or etching and the other is the technique of separating the front side portion and the rear side portion of the first article along the separation layer formed in the first article. When the latter technique is used, the unnecessary part can be used as a first or second article once again because it maintains the profile of a wafer after the removal. The unnecessary part can be removed by heat-treating the assembly, blowing fluid that may be liquid or gas to a lateral side of the assembly or mechanically peeling it off from the rest.

The surface of the silicon layer (SOI layer) of the assembly (SOI substrate) that is now free from the unnecessary part is rather rough, showing voids, pores of the porous layer and/or undulations caused by the grinding or etching operation. Therefore, in Step S5, an upper portion of the silicon layer showing a rough

26 JUN 2002

surface is smoothed by heat-treating (annealing by means of hydrogen) it. Then, the surface roughness of the etched silicon layer is smoothed to a level of surface roughness of less than 0.2nm (in a 1 m square area) due to the smoothing effect of the etching operation. If the etching is conducted under optimized conditions, the surface roughness can be reduced to less than 0.15nm, in some cases to less than 0.1nm.

FIG. 12 is a flow chart for preparing an SOI substrate typically by means of a SIMOX process.

Firstly in Step S11, an Si wafer is prepared as starting material.

Then, in Step S12, oxygen ions are implanted typically with a dosing rate of about $2x10^{17}cm^{-2}$ to $4x10^{18}cm^{-2}$, using an acceleration voltage of between 100eV and 300eV.

Subsequently, in Step S13, the wafer implanted with oxygen ions is heat-treated at temperature between 1,000°C and 1,400°C to produce a buried oxide film.

Then, in Step S14, the surface oxide film is removed from the surface of the SOI layer, if such an oxide film has been formed.

The surface of the SOI layer of the obtained SOI substrate shows undulations caused by the oxygen ion implantation (Step S12) and the formation of the buried oxide film (Step S13) if a polished wafer is used as starting material. Thus, in Step S15, the wafer is

26 JUN 2002

subjected to a heat treatment operation (annealing operation using hydrogen) in a manner as described above to remove an upper portion of the SOI layer having undulations. After the etching, the surface of the SOI layer shows a surface roughness of less than 0.4nm (Rrms) in a 1μm square area and less than 1.5nm (Rrms) in a 50μm square area.

Of the above described methods of preparing a semiconductor article according to the invention, that of preparing an SOI substrate by means of the cleave process using hydrogen ion implantation will be discussed in greater detail by referring to FIGS. 13A through 13D.

In Step S21 shown in FIG. 13A, at least the surface of an Si wafer 31 that is the first article is thermally oxidized to produce a silicon oxide layer that becomes a buried insulation film 22 and then hydrogen or inert gas ions are implanted typically with a dosing rate of about $1x10^{16}cm^{-2}$ to $1x10^{19}cm^{-2}$, using an acceleration voltage of between 10keV and 500keV. Ions may be implanted by means of an ion implanter or, alternatively, from hydrogen or inert gas plasma, by utilizing the potential difference between the plasma and the wafer. As a result, a separation layer 32 is produced (FIG. 13A).

Then, in Step S22 shown in FIG. 13B, another Si wafer 21 that is a second article is prepared by

26 JUN 2002

removing the natural oxide film, if any, on the surface to be bonded thereof before the two Si wafers are bonded together with the Si surface held in contact with the surface of the insulation film 22 to produce an assembly.

Subsequently, in Step S23 shown in FIG. 13C, the assembly is heat-treated in an oxidizing atmosphere and separated into two parts along the separation layer 32. For separating the assembly into two parts, fluid (liquid or gas) may be applied to a lateral side of the assembly under high pressure until the separation layer that is a mechanically weak brittle layer is destroyed and the wafer 31 is peeled off (separated) from the assembly, leaving the silicon film 23 on the wafer 21. Alternatively, fine bubbles will be generated by hydrogen or inert gas ions to grow in the separation layer so that consequently the wafer 31 may be separated from the assembly, leaving the silicon film 23 on the wafer 21, if temperature higher than 500°C is used for the heat treatment to be conducted in an oxidizing atmosphere simultaneously with or after the bonding step.

The wafer 31 separated from the assembly can be used as a first or second article once again because it maintains the profile of a wafer after the removal, although itsheight is reduced by the thickness of the silicon film 23.

26 JUN 2002

For reusing the separated wafer 31, the surface exposed as a result of the separation is polished and single crystal silicon film is made to grow thereon through epitaxial growth.

After the separation, the silicon film 25 shows a rough surface with undulations caused by fine bubbles (fine voids). Therefore, in Step S24 shown in FIG. 13D, it is arranged vis-a-vis a non-oxidized silicon plane and heated-treated in a hydrogen-containing reducing atmosphere to smooth an upper portion of the silicon film 23 including the rough surface by means of a method according to the invention in a manner as described above.

Since the wafer 21 carries a silicon oxide film 24 on the rear surface thereof as a result of the heat treatment conducted in an oxidizing atmosphere in the example of FIGS. 13A through 13D, the silicon oxide film may be left on the rear surface of the SOI substrate after the end of Step S23. Therefore, the silicon oxide film is removed by means of an etchant such as hydrofluoric acid, using the surface of the silicon film 25 as mask. Then, thereafter, a number of such SOI substrates can be simultaneously subjected to an etching process in an apparatus according to the invention as described above and illustrated in FIG. 6, 9 or 10.

Alternatively, the heat treatment for bonding the

two substrates may be conducted in a non-oxidizing atmosphere so that an oxide film 24 may be formed on the rear surface during the bonding process. Then, a non-oxidized silicon rear surface can be obtained by removing the natural oxide film, if any, before the annealing operation using hydrogen.

Now, a method of preparing a semiconductor article by means of an epitaxial layer transfer process will be discussed in detail by referring to FIGS. 14A through 14F.

Firstly, in Step S31 shown in FIG. 14A, an Si single crystal substrate 31 is prepared as a first article and a layer having a porous structure 33 is formed at least on the principal front surface thereof. Porous Si can be produced by anodizing the Si substrate in an HF solution. Such a porous layer shows a sponge-like structure, where pores with a diameter of about 10^{-1}nm to 10nm are arranged with intervals of about 10^{-1} to 10nm. While the density of single crystal Si is 2.33g/cm^3, that of porous Si is variable and can be made to fall within a range between 2.1 and 0.6g/cm^3 by regulating the concentration of the HF solution within a range between 50 and 20% and also regulating the current density and the rate at which alcohol is added to the reaction system. The porosity of the porous layer can be controlled by modulating the specific resistance and the conductivity type of the

26 JUN 2002

portion of the substrate to be made porous. An Si substrate having the p-type conductivity will show a higher porosity when it is a non-degenerate substrate (P^-) than when it is a degenerate substrate (P^+) under same anodizing conditions because the former shows a pore density higher than the latter by a digit, although it may show a small pore diameter. In short, the porosity of the Si substrate can be controlled by regulating these conditions and using an appropriate method selected out of a number of feasible methods. The porous layer 33 may be a single layer or a multilayer structure comprising a number of layers with different porosities. When ions are implanted in such a way that their projection range is confined within the porous layer that is produced by anodization, bubbles will be formed in the pore walls located near the projection range and consequently the porosity of the layer can be raised. The ion implantation process may be conducted before or after the step of forming the porous layer by anodization or even after the step of forming a single crystal semiconductor layer on the porous layer 33.

Then, in Step S32 shown in FIG. 14B, at least a non-porous single crystal semiconductor layer 23 is formed on the porous layer. Such a non-porous single crystal semiconductor layer 23 may be a single crystal Si layer formed by epitaxial growth, a layer formed by

transforming a surface layer of the porous layer 33 into a non-porous layer or some other appropriate layer. If a silicon oxide layer 22 is formed on the single crystal Si layer 23 by thermal oxidation, the interface of the single crystal silicon layer and the buried oxide film will be a suitable interface formed by thermal oxidation with a low boundary energy level. In Step S33 shown in FIG. 14C, the principal surface (bonding surface) of the semiconductor substrate where said non-porous single crystal Si layer 23 has been formed is held in close contact with the front surface (bonding surface) of a second substrate 21. It is desirable to cleanse the surfaces in order to remove any adherent foreign objects from them before they are brought into close contact with each other. The second substrate may be an Si substrate, a substrate obtained by forming a silicon oxide film on an Si substrate, a light transmitting substrate typically made of quartz or a sapphire substrate, although it is not limited thereto so long as the surface to be bonded is sufficiently flat and smooth. While the second substrate is bonded to the first substrate with an insulation layer 22 interposed therebetween according to the illustration, the insulation layer 22 may not necessarily be used.

For bonding the two substrates, an insulator thin plate may be sandwiched between the first and second

26 JUN 2002

substrates to produce a three-layered structure.

Subsequently, the unnecessary portion on the rear surface of the first substrate 31 and the porous layer 33 are removed to expose the non-porous single crystal Si layer 23. Either of the above described two techniques is used for this step of exposing the non-porous single crystal Si layer 23, although some other technique may alternatively be used.

With the first technique, the first substrate 21 is removed from the rear side to expose the non-porous layer 33 (Step S34 shown in FIG. 14D).

Thereafter, the porous layer 33 is removed to exposed the non-porous single crystal silicon layer 23 (Step S35 shown in FIG. 14E).

It is preferable to remove the porous layer by selective etching. Porous silicon can be selectively etched at a rate 10^5 times greater than the rate of etching non-porous single crystal silicon when a mixture solution containing at least hydrofluoric acid and hydrogen peroxide is used. A surface active agent may be added to the etching solution in order to prevent bubbles from adhering to the surface. Alcohol such as ethyl alcohol may preferably be used as surfactant. The selective etching process may be omitted when the porous layer is very thin.

With the second technique, the substrates are separated along the porous layer 33 that operates as

26 JUN 2002

separation layer to produce a profile as shown in FIG. 14D for Step S34. The separation may be realized by the use of external force. Methods that can be used for the separation include among others application of external force such as pressure, tensile force or shearing force or the use of a wedge, application of ultrasonic waves, the use of heat, the use of a technique of producing internal pressure in the porous Si by oxidizing it and expanding it from the periphery, the use of pulsating heat for producing thermal stress in or softening the porous Si and ejection of a fluid jet stream such as water jet or gas jet.

Preferably, the separation layer comprises at least two layers having different porosities.

Subsequently, in Step S35, the residual porous layer 33 left on the front surface of the second substrate 21 is removed by etching. The technique used above for exposing the porous layer 33 by etching can also be used for etching out the residual porous layer 33. If the residual porous silicon layer 33 left on the second substrate 21 is very thin and uniform, this wet etching process using hydrofluoric acid and hydrogen peroxide may be omitted.

Then, in Step S36 shown in FIG. 14F, the assembly is subjected to heat treatment in a hydrogen-containing reducing atmosphere in order to anneal the undulated upper portion 25 of the single crystal Si layer 23. At

26 JUN 2002

the same time, this step gives rise to the effect of reducing the boron concentration in the single crystal silicon layer and smoothing the surface of the assembly.

In a semiconductor substrate obtained by the above described method of the invention, a flat, uniform and thin single crystal Si film 23 is formed on the entire surface of the second substrate 21 with an insulation layer 22 interposed therebetween to take a large areas. Such a semiconductor substrate can advantageously be used for manufacturing electronic devices that are insulated and isolated from each other.

The residual porous layer left on the surface of separation of the separated first Si single crystal substrate 31 is removed and the exposed surface is smoothed if it is unacceptably rough. Then, it will be used as a first Si single crystal substrate for another time or as a second substrate 21 to be used subsequently.

No silicon oxide is formed on the rear surface of the substrate 21 in the example of FIGS. 14A through 14F. However, when the substrate 21 itself is made of silicon oxide such as fused quartz, it may be sufficient to form a film of Si, SiC or SiN on the rear surface of the substrate 21 after Step S35, using the silicon film 23 as mask, or annealing the substrate by means of hydrogen, using a tray of SiC or SiC coated

26 JUN 2002

carbon.

FIGS. 15A and 15B schematically show the silicon surface of an article before and after a heat treatment process according to the invention.

In FIGS. 15A and 15B, W3 denotes a cross section of the article before the etching process, whereas W4 denotes a cross section of the article after the etching process.

If silicon is not located vis-a-vis silicon oxide, silicon-containing gaseous substances that typically include SiH_2 and are produced from the silicon surface would not be consumed so that the silicon gasifying reaction, or etching, taking place on the surface will be suppressed once the saturation vapor pressure is reached. Thus, the effect of etching silicon can be suppressed by reducing the rate of gas flow near the silicon film to maintain the vapor pressure of the silicon-containing gaseous substances produced from the silicon surface at a high level.

When a 1μm square area was observed through an atomic force microscope before the heat treatment process, the root mean square (Rrms) of surface roughness was about 0.2nm to 20nm.

As a result of an etching process according to the invention, the rough surface was smoothed to show an Rrms of as low as about 0.07nm to 0.15nm, which corresponds to the surface roughness of a polished Si

wafer or a surface that is more smooth than it. In FIGS. 15A and 15B, h denotes the peak to valley distance, p denotes the gap between two adjacent peaks and t denotes the etching depth. In known comparable processes, the thickness t of film 23 will be reduced when the surface of the article is polished and smoothed. However, with a process according to the invention, there will be no reduction in the film thickness because the etching rate can be held to about 0.01nm at 1,150°C.

According to the invention, after the etching process, the surface roughness is reduced to about one third of that of the unetched surface. Thus, a highly undulated silicon surface having a peak to valley distance h as large as several nanometers to tens of several nanometers and a gap between two adjacent peaks p as large as several nanometers to hundreds of several nanometers can be smoothed to show an h value not greater than 2nm, preferably not greater than 0.4nm by heat treatment.

This smoothing phenomenon may be explained as a rearrangement of the surface. On a rough surface, there may exist innumerable ridges showing a high energy surface state and planes with planar bearings of higher orders may be exposed to the surface relative to the planar bearings of the crystal layer. The surface energy of such an area is higher than the surface

26 JUN 2002

energy that relies on the planar bearing of the single crystal surface. In a heat treatment process conducted in a hydrogen-containing reducing atmosphere, it may be safely assumed that the energy barrier against the mobilization of surface Si atoms is lowered typically by the reducing effect of hydrogen so that Si atoms excited by thermal energy are mobilized to rearrange the surface into a flat and smooth surface that shows a low energy surface state. The lower the planar bearing index of the single crystal surface, the more the planarizing and smoothing effect of the present invention will be promoted.

(Example 1: epitaxial layer transfer/horizontal furnace/SiO_2 counter-surface)

For each specimen, the surface of a 6-inch boron-doped Si wafer having a specific resistance of 0.015 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 10μm thick porous silicon layer on the wafer surface. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour. As a result, a very thin oxide film is formed on the surface of the porous layer and also on the wall surfaces of the pores. Subsequently, the silicon wafer was dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on the surface of the porous layer and on the wall

surfaces of the pores near the surface. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in an epitaxial growth system and heat-treated at 1,100°C in a hydrogen atmosphere to shut almost all the pores on the surface of the porous silicon. Then, a single crystal silicon film was formed on the porous silicon to an average thickness of 300nm±5nm by adding dichlorosilane as silicon source gas to the hydrogen gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single crystal silicon film came to show a thickness of 210nm. Meanwhile, a second silicon wafer was prepared and each of the wafers was subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface (bonding surface). Then, the two silicon wafers were bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 1,100°C for 1 hour to enhance the bonding strength at the interface. An atmosphere of a mixture of nitrogen and oxygen was used for the heat treatment. Then, the first silicon wafer of the

silicon wafer assembly was ground from the rear surface until the porous silicon became exposed. Then, the silicon wafer assembly was dipped into a mixture solution of HF and hydrogen peroxide to etch out the porous silicon. The assembly was then subjected to a wet cleansing operation and cleansed well. It was found that the single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

The film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±5nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square of surface roughness (Rrms) was 10.1nm for the 1μm square areas and 9.8nm for the 50μm square areas. When the boron concentration was measured by means of secondary ion mass spectrography (SIMS), it was found that the boron concentration in the single crystal silicon film was $1.2 \times 10^{18}/cm^3$.

The silicon oxide formed on the rear surface of the SOI wafer was preliminarily cleansed by hydrofluoric acid and removed by etching. Then, the wafer was placed in a horizontal heat treatment furnace comprising a cylindrical furnace tube made of fused

26 JUN 2002

quartz. Gas was made to flow from an end to the other of the furnace tube. The specimens of SOI wafers were tested in different modes of arrangement as will be described below. FIGS. 16A through 16E schematically show the different modes of arrangement. Throughout the drawings, 21 denotes a second silicon wafer operation as support substrate, 22 denotes a silicon oxide film which is a buried insulation film and 23 denotes a single crystal silicon film.

Specimen A: FIG. 16A: An SOI wafer W was horizontally placed in the furnace.

Specimen B: FIG. 16B: An SOI wafer W was horizontally placed in the furnace and a silicon wafer carrying no oxide film thereon was placed above the SOI wafer. The distance separating the two wafers was about 10mm.

Specimens C, C': FIG. 16C: A pair of SOI wafers are arranged inclinedly and in parallel with each other in the furnace.

Specimens D, D': FIG. 16D: A pair of SOI wafers are vertically arranged in parallel with each other in such a way that the surfaces carrying a single crystal silicon film 23 of the wafers are located vis-a-vis and the centers of the wafers agree with the center line of the furnace.

Specimens E, E': FIG. 16E: A pair of SOI wafers are vertically arranged in parallel with each other in such a way that the surfaces carrying a single crystal

26 JUN 2002

silicon film 23 of the wafers are directed to the upstream and the centers of the wafers agree with the center line of the furnace. All the wafers were held and supported by respective quartz jigs (not shown).

For each specimen, after replacing the atmosphere in the furnace by hydrogen, the temperature was raised to 1,100°C and held to that level for 4 hours before the temperature was made to fall. Then, the atmosphere in the furnace was replaced by nitrogen and the wafer specimen was taken out to observe the film thickness of the single crystal silicon film for another time. The reduction in the film thickness on each of the specimens is shown below. The hydrogen gas flow rate was 5slm. The film thickness was measured at intra-planar 10mm lattice points and the obtained values were averaged.

26 JUN 2002

	etched height	film thickness	deviation
Specimen A:	15.2nm	193.8nm	±9nm
Specimen B:	3nm	206mm	±5.2nm
Specimen C:	10.4nm	199.1nm	±8nm (upstream wafer)
Specimen C':	1.7nm	208nm	±5nm (downstream wafer)
Specimen D:	1.4nm	208.3nm	±5nm (upstream wafer)
Specimen D':	1.2nm	208.5mm	±5.1nm (downstream wafer)
Specimen E:	12.4nm	197.3nm	±8.5nm (upstream wafer)
Specimen E':	1.1nm	208.7nm	±5nm (downstream wafer)

The decrease in the film thickness of the SOI wafer was less than 2nm for all the wafers when silicon was used for the counter-surface. On the other hand, when no silicon was used for the counter-surface but the inner surface of the cylindrical furnace tube made of fused quartz was used to operate as counter-surface, the decrease in the film thickness produced by etching exceeded 10nm for the specimens A, C (upstream wafer) and E (upstream wafer). Thus, by using silicon for the counter-surface, the etched height was reduced to less than 1/5 of the loss of height produced when non-oxidized silicon counter-surface is not used. Variations in the film thickness were not worsened from those observed prior to the heat treatment.

After the above heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness

26 JUN 2002

of each of the specimens is shown below.

	1μm square area	50μm square area
Specimen A:	0.11nm	0.35nm
Specimen B:	0.13nm	0.36nm
Specimen C':	0.11nm	0.33nm
Specimen D:	0.13nm	0.35nm (upstream wafer)
Specimen D':	0.13nm	0.35nm (downstream wafer)
Specimen E':	0.12nm	0.32nm
marketed Si wafer:	0.13nm	0.31nm (for reference)

The above data indicate that the specimens were smoothed to the level of commercially available polished silicon wafers.

After the above heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices.

(Example 2: epitaxial layer transfer/vertical furnace/various boats/oxide film rear surface)

For each specimen, the surface of a 8-inch boron-doped Si wafer having a specific resistance of 0.017 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 10μm thick porous silicon

layer on the wafer surface. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour and subsequently dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on and near the surface of the porous silicon layer. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in an epitaxial growth system and heat-treated at 1,100°C in a hydrogen atmosphere by adding silane gas at a very small rate to shut almost all the pores on the surface of the porous silicon. Then, a single crystal silicon film was formed on the porous silicon to an average thickness of 310nm±5nm by adding silane as silicon source gas to the hydrogen gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single crystal silicon film came to show a thickness of 210nm. Meanwhile, a second silicon wafer was subjected to a thermal oxidation process to form a 200nm thick silicon oxide film on the entire surface thereof and each of the wafers was subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface. Then, the two silicon wafers

26 JUN 2002

were bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 1,100°C for 1 hour to enhance the bonding strength at the interface. The temperature of the atmosphere of the heat treatment was raised in a mixture gas of nitrogen and oxygen and then replaced by combustion gas of oxygen and nitrogen. The temperature was held to 1,100°C for 1 hour and then lowered in a nitrogen atmosphere. Then, the first silicon wafer of the silicon wafer assembly was ground from the rear surface until the porous silicon became exposed. Then, the silicon wafer assembly was dipped into a mixture solution of HF and hydrogen peroxide to etch out the porous silicon. The assembly was then subjected to a wet cleansing operation and cleansed well. It was found that the single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

The film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±4.3nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 10.1nm for the 1μm square areas

and 9.8nm for the 50μm square areas. When the boron concentration was measured by means of secondary ion mass spectrography (SIMS), it was found that the boron concentration in the single crystal silicon film was $1.2x10^{18}/cm^3$.

The obtained SOI wafers were placed in a vertical heat treatment furnace comprising a furnace tube made of quartz and having a configuration as shown in FIG. 9 without removing the silicon oxide film on the rear surface. Gas was made to flow from above to below in the furnace.

A commercially available bulk Si 8-inch wafer was used as counter-surface constituting member. As shown in FIG. 9, the wafers W were arranged horizontally on a SiC boat 4 in such a way that the silicon oxide rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A bulk Si 8-inch wafer 3 was arranged on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,100°C and held to that level for 4 hours before the temperature was lowered to take out the wafers and observe the film thickness of

the SOI of each specimen. The decrease in the film thickness of each of the SOI wafers was not greater than 1nm.

Then, the boat supporting the wafers was replaced by a boat made of vitreous silica and a similar experiment was conducted to fined that one of the wafers W had been etched by 8nm at maximum in an area supported by the boat, although the etched height was less than 1nm in the central area of all of the wafers as in the case of the use of an SiC boat. Thus, it was found that a boat having a surface of non-oxidized silicon, SiO_2 for example, is preferably used for the purpose of the invention.

When the silicon oxide film on the rear surface of each of the wafers was not removed before the heat treatment so that the SOI layer was made to face a silicon oxide rear surface and heat-treated in a hydrogen atmosphere as in the above experiment, the decrease in the film thickness of the SOI layer facing another SOI wafer was as large as 9nm and only the SOI wafer facing the uppermost silicon wafer showed a decrease of less than 1nm in the film thickness by etching. In short, the etching effect could be suppressed to about 1/10 by using silicon for the counter-surface.

FIG. 17 shows the result of the above experiment. More specifically, FIG. 17 shows the location

dependency of the film thickness reduction of the SOI layer of wafers in the furnace in a heat treatment process according to the invention. In FIG. 17, the horizontal axis represents the numerical order of arrangement of the wafers in the furnace as counted from above and the vertical axis represents the decrease (nm) in the film thickness due to heat treatment. In FIG. 17, F denotes the data obtained when the silicon oxide film on the rear surface of each SOI wafer had been removed before the SOI layer of the wafer was arranged vis-a-vis the silicon rear surface of another SOI wafer and G denotes the data obtained for comparison when the SOI layer of each SOI wafer was arranged vis-a-vis the silicon oxide rear surface of another SOI wafer that had not been removed. Note that a silicon wafer (dummy wafer) wasarranged above the fist SOI wafer in order to maintain the high temperature in the furnace and therefore the front surface of the first SOI wafer was facing the silicon rear surface of the dummy wafer.

As seen from FIG. 17, the decrease in the film thickness was less than 1nm only for the first SOI wafer arranged vis-a-vis a dummy Si wafer and about 10nm for all the SOI layers of the remaining SOI wafers when the silicon oxide was not removed from the rear surface.

After the heat treatment, the specimens were

observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.11nm for a 1μm square area and 0.35nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices. (Example 3: epitaxial layer transfer/vertical furnace/quartz tray)

For each specimen, the surface of an 8-inch boron-doped Si wafer having a specific resistance of 0.017 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 10μm thick porous silicon layer on the wafer surface. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour and subsequently dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on and near the surface of the porous silicon layer. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in an epitaxial growth system and

heat-treated at 1,100°C in a hydrogen atmosphere to shut almost all the pores on the surface of the porous silicon. Then, a single crystal silicon film was formed on the porous silicon to an average thickness of 310nm±5nm by adding dichlorosilane as silicon source gas to the hydrogen gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single crystal silicon film came to show a thickness of 210nm. This wafer and a second wafer of 200nm were separately subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface. Then, the two silicon wafers were bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 1,100°C for 1 hour to enhance the bonding strength at the interface. A mixture gas of nitrogen and oxygen was used for the atmosphere of the heat treatment and heated before it was replaced by combustion gas of oxygen and hydrogen and held to 1,100°C. Thereafter, the temperature was lowered in a nitrogen atmosphere. Then, the first silicon wafer of the silicon wafer assembly was ground from the rear surface until the

porous silicon became exposed. Then, the silicon wafer assembly was dipped into a mixture solution of HF and hydrogen peroxide to etch out the porous silicon. The assembly was then subjected to a wet cleansing operation and cleansed well. The single crystal silicon film produced by epitaxial growth had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

For each of the specimens, the film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±7nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 10.1nm for the 1μm square areas and 9.8nm for the 50μm square areas. When the boron concentration was measured by means of secondary ion mass spectrography (SIMS), it was found that the boron concentration in the single crystal silicon film was $1.2x10^{18}cm^3$.

All the obtained SOI wafers were placed on respective SiC trays as shown in FIG. 7 and put into a vertical heat treatment furnace shown in FIG. 9 and comprising a furnace tube made of fused quartz with a loading chamber. Inert gas was introduced into the

loading chamber in which the wafers and trays were places. Inert gas was made to flow from above to below in the furnace. The wafers were transferred from the loading chamber to the furnace without exposing the inside of the furnace to oxidizing atomosphere. The wafers were arranged horizontally on the respective SiC trays in such a way that the rear surface of each of the trays supporting an SOI wafer thereon faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available silicon wafer 3 was arranged on a tray, which was then placed on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,180°C and held to that level for 1 hour before the temperature was lowered to take out the wafers and observe the film thickness of the SOI of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm for all the SOI wafers.

On the other hand, after a similar heat treatment operation conducted also in a hydrogen atmosphere where the SiC trays were replaced with SiO_2 trays and the SOI layer of each SOI wafer was made to face silicon oxide,

it was found that the decrease in the film thickness of the SOI layer facing an SOI wafer was as large as 40nm.

Thus, although the wafers did not carry a silicon oxide film on the rear surface, the silicon layer was etched as a result of using a quartz tray for each specimen to provide a counter-surface for the wafer located immediately therebelow.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.11nm for a 1μm square area and 0.30nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $1x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices.

(Example 4: WJ separation/epitaxial layer transfer)

For each specimen, the surface of an 8-inch boron-doped Si wafer having a specific resistance of 0.017 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 6μm thick porous silicon layer on the wafer surface. To be more accurate, the

porous silicon layer included a 1μm thick highly porous layer having a porosity of about 60% and a 5μm thick lowly porous layer having a porosity of 20% located on the highly porous layer, which layers were produced by varying the electric current. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour and subsequently dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on the surface of the low porosity porous layer and the wall surfaces of the pores located near that surface. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in an epitaxial growth system and heat-treated at 1,100°C in a hydrogen atmosphere by adding silane gas at a very small rate to shut almost all the pores on the surface of the porous silicon. Then, a single crystal silicon film was formed on the porous silicon to an average thickness of 310nm±5nm by adding dichlorosilane as silicon source gas to the hydrogen gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single crystal silicon film came to show a thickness of 210nm. Meanwhile, a second silicon wafer was subjected to a

26 JUN 2002

thermal oxidation process to form a 200nm thick silicon oxide film on the entire surface thereof and each of the wafers was subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface. Then, the two silicon wafers were bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 1,100°C for 1 hour to enhance the bonding strength at the interface. An atmosphere of a mixture of nitrogen and oxygen was used for the heat treatment. Then, the silicon wafer assembly was separated along the highly porous layer under the fluid wedge effect by applying a high pressure water jet stream a lateral side of the assembly to expose the porous layer. Then, the second silicon wafer was dipped into a mixture solution of HF and hydrogen peroxide to remove the residual porous silicon by selective etching. It was then subjected to a wet cleansing operation and cleansed well. It was found that the single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

For each of the specimens, the film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±7nm. When a 1μm square area and a 50μm

26 JUN 2002

square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 10.1nm for the 1μm square areas and 9.8nm for the 50μm square areas. When the boron concentration was measured by means of secondary ion mass spectrography (SIMS), it was found that the boron concentration in the single crystal silicon film was $1.2x10^{18}/cm^3$.

The silicon oxide film on the rear surface of all the obtained SOI wafers was etched out in advance by means of hydrofluoric acid and the SOI wafers were put into a vertical heat treatment furnace comprising a furnace tube made of fused quartz. Gas was made to flow from above to below in the furnace. The wafers were arranged horizontally on a SiC boat as shown in FIG. 9 in such a way that the rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of about 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available bulk silicon wafer from which the natural silicon film, if any, had been removed was arranged on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by

hydrogen, the temperature in the furnace was raised to 1,100°C and held to that level for 4 hours before the temperature was lowered to take out the wafers and observe the film thickness of the SOI of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm.

When the silicon oxide film on the rear surface of each of the wafers was not removed before the heat treatment so that the SOI layer was made to face a silicon oxide rear surface and heat-treated in a hydrogen atmosphere as in the above experiment, the decrease in the film thickness of the SOI layer facing another SOI wafer was as large as 9nm and only the SOI wafer facing the uppermost silicon wafer showed a decrease of less than 1nm in the film thickness by etching. In short, the etching effect could be suppressed to about 1/10 by using silicon for the counter-surface.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.12nm for a 1μm square area and 0.34nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens

26 JUN 2002

was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices.

(Example 5: BESOI/vertical furnace/SiC boat)

For each specimen, an 8-inch boron-doped Si wafer having a specific resistance of 0.007 Ωcm and a (100) orientation was placed in an epitaxial growth system and heat-treated at 1,100°C in a hydrogen atmosphere. After lowering the temperature to 900°C, a single crystal silicon film was produced to an average film thickness of 310nm±5nm by using hydrogen gas, to which dichlorosilane was added as silicon source gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single crystal silicon film came to show a thickness of 210nm. Meanwhile, a second silicon wafer was subjected to a thermal oxidation process to form a 200nm thick silicon oxide film on the entire surface thereof and each of the wafers was subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface. After activating the surfaces (bonding surfaces) of the wafers by means of an oxygen

plasma process, the two silicon wafers were washed with water and bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 400°C for 10 hours to enhance the bonding strength at the interface. A nitrogen atmosphere was used for the heat treatment. Then, the silicon wafer assembly was scraped from the rear surface of the first silicon wafer until thickness of the first silicon wafer was reduced to about 5μm. Subsequently, the P^+ layer was selectively etched by dipping the silicon wafer assembly in a 1:3:8 mixture solution of hydrofluoric acid, nitric acid and acetic acid. The single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

For each of the specimens, the film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±20nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 2nm for the 1μm square areas and 2.2nm for the 50μm square areas.

The silicon oxide film on the rear surface of all

the obtained SOI wafers was etched out in advance by means of hydrofluoric acid and the SOI wafers were put into a vertical heat treatment furnace comprising a furnace tube made of fused quartz. Gas was made to flow from above to below in the furnace. The wafers were arranged horizontally on a SiC boat as shown in FIG. 9 in such a way that the rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of about 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available bulk silicon wafer from which the natural silicon film, if any, had been removed was arranged on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,100°C and held to that level for 4 hours before the temperature was lowered to take out the wafers and observe the film thickness of the SOI of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.11nm for a 1μm

square area and 0.35nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices.

(Example 6: cleave process by hydrogen ion implantation/vertical furnace/SiC boat)

For each specimen, the surface of an 8-inch boron-doped Si wafer having a specific resistance of 10 Ωcm and a (100) orientation was oxidized by 400nm and hydrogen ions were implanted into the wafer under the conditions of 50KeV and $4x10^{16}/cm^2$. The silicon wafer and a second silicon wafer were separately subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface (bonding surface). Then, the two silicon wafers were bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 800°C for 10 hours in a heat treatment furnace to enhance the bonding strength at the interface. A nitrogen atmosphere was used for the heat treatment. During the heat treatment, the silicon wafer assembly was

26 JUN 2002

separated along the depth corresponding to the projection range of implanted ions. The single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

For each of the specimens, the film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±10nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 9.4nm for the 1μm square areas and 8.5nm for the 50μm square areas.

The silicon oxide film on the rear surface of all the obtained SOI wafers was etched out in advance by means of hydrofluoric acid and the SOI wafers were put into a vertical heat treatment furnace comprising a furnace tube made of fused quartz. Gas was made to flow from above to below in the furnace. The wafers were arranged horizontally on a SiC boat as shown in FIG. 9 in such a way that the rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of about 6mm, the center of each of the wafers agreeing

with the center line of the furnace tube. A commercially available bulk silicon wafer from which the natural silicon film, if any, had been removed was arranged on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,150°C and held to that level for 1.5 hours before the temperature was lowered to take out the wafers and observe the film thickness of the SOI of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.11nm for a 1μm square area and 0.35nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices.

(Example 7: SIMOX/vertical furnace/SiC boat)

For each specimen, oxygen ions were implanted into

the surface of an 8-inch boron-doped Si wafer having a specific resistance of 10 Ωcm and a (100) orientation under the conditions of 550°C, 180KeV and $4x10^{17}/cm^2$. The silicon wafer was placed in a heat treatment furnace and heat-treated in a mixture gas of $Ar+O_2$ at 1,350°C for 20 hours to produce a buried oxide film.

For each of the specimens, the film thickness of the transferred single crystal silicon film formed on the buried oxide film was measured at intra-planar 10mm lattice points to find that the average film thickness was 200nm with a deviation of ±10nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 0.5nm for the 1μm square areas and 2nm for the 50μm square areas to prove that the surface roughness was increased by the oxygen ion implantation. When the boron concentration was measured by means of secondary ion mass spectrography (SIMS), it was found that the boron concentration in the single crystal silicon film was $5x10^{17}$/cm3for all the specimens.

The silicon oxide film on the rear surface of all the obtained SOI wafers was etched out in advance by means of hydrofluoric acid and the SOI wafers were put into a vertical heat treatment furnace comprising a furnace tube made of fused quartz. Gas was made to

26 JUN 2002

flow from above to below in the furnace. The wafers were arranged horizontally on a SiC boat as shown in FIG. 9 in such a way that the rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of about 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available bulk silicon wafer from which the natural silicon film, if any, had been removed was arranged on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,150°C and held to that level for 1.5 hours before the temperature was lowered to take out the wafers and observe the film thickness of the SOI of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.3nm for a 1μm square area and 1.5nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the

single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices. (Example 8: non-porous layer transfer/vertical furnace/SiC boat)

For each specimen, the surface of an 8-inch boron-doped Si wafer having a specific resistance of 0.017 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 10μm thick porous silicon layer on the wafer surface. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour and subsequently dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on and near the surface of the porous silicon layer. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in a vertical heat treatment furnace and heat-treated at 1,100°C in a hydrogen atmosphere to shut almost all the pores on the surface of the porous silicon and form a very thin non-porous single crystal silicon film on the surface by modifying the surface of the porous layer to non-porous. This silicon wafer and a second silicon wafer that had been subjected to a thermal oxidation process to form a 200nm thick silicon

26 JUN 2002

oxide film on the entire surface thereof were then separately subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface. Thereafter, the two silicon wafers were cleansed in a wet cleansing process to produce clean surfaces and bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 1,100°C for 1 hour to enhance the bonding strength at the interface. A mixture gas of nitrogen and oxygen was used for the atmosphere of heat treatment and heated before it was replaced by combustion gas of oxygen and hydrogen and held to 1,100°C for 1 hour. Thereafter, the temperature was lowered in a nitrogen atmosphere. Then, the silicon wafer assembly was scraped from the rear surface of the first silicon wafer to expose the porous silicon. Then, the silicon wafer assembly was dipped into a mixture solution of HF and hydrogen peroxide to etch out the porous silicon layer. It was then subjected to a wet cleansing operation and cleansed well. It was found that the non-porous single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

For each of the specimens, the film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find

that the average film thickness was 10nm. When a 1μm square area and a 50μm square area of the surface were observed through an atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 10.1nm for the 1μm square areas and 9.8nm for the 50μm square areas.

The silicon oxide film on the rear surface of all the obtained SOI wafers was etched out in advance by means of hydrofluoric acid and the SOI wafers were put into a vertical heat treatment furnace comprising a furnace tube made of fused quartz. Gas was made to flow from above to below in the furnace. The wafers were arranged horizontally on a SiC boat as shown in FIG. 9 in such a way that the rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of about 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available bulk silicon wafer from which the natural silicon film, if any, had been removed was arranged on top of the SOI wafers,keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1100°C and held to that level for 4 hours before the temperature was lowered to take out the wafers and

observe the film thickness of the SOI of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm.

When the silicon oxide film on the rear surface of each of the wafers was not removed before the heat treatment so that the SOI layer was made to face the silicon oxide on the rear surface a wafer and heat-treated in a hydrogen atmosphere as in the above experiment, the decrease in the film thickness of the SOI layer facing another SOI wafer was as large as 5nm and scattered pit-like spots of unetched silicon oxide were observed. Only the SOI wafer facing the uppermost silicon wafer showed a decrease of less than 1nm in the film thickness by etching and were free from pit-like spots. In short, the etching effect could be suppressed and the generation of pit-like spots could be eliminated by using silicon for the counter-surface.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.11nm for a 1μm square area and 0.35nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers.

(Example 9: epitaxial layer transfer on vitreous silica/horizontal furnace/SiC tray)

For each specimen, the surface of an 8-inch

26 JUN 2002

boron-doped Si wafer having a specific resistance of 0.017 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 10μm thick porous silicon layer on the wafer surface. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour and subsequently dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on and near the surface of the porous silicon layer. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in an epitaxial growth system and heat-treated at 1,100°C in a hydrogen atmosphere, adding silane gas at a very small rate, to shut almost all the pores on the surface of the porous silicon layer. Then, a single crystal silicon film was formed on the porous silicon to an average thickness of 310nm±5nm by adding dichlorosilane as silicon source gas to the hydrogen gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single crystal silicon film came to show a thickness of 210nm. Then, this silicon wafer and a second silicon wafer on which a silicon oxide film was formed by

thermal oxidation to a thickness of 200nm over the entire surface were separately subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface (bonding surface). The surfaces (bonding surfaces) were activated by nitrogen plasma before they were washed with water and dried. The two silicon wafers were then bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 400°C for 10 hours to enhance the bonding strength at the interface. Then, the silicon wafer assembly was scraped from the rear surface of the first silicon wafer to expose the porous silicon layer. Then, the silicon wafer assembly was dipped into a mixture solution of HF and hydrogen peroxide to etch out the porous silicon. It was then subjected to a wet cleansing operation and cleansed well. It was found that the single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer.

For each of the specimens, the film thickness of the transferred single crystal silicon film was measured at intra-planar 10mm lattice points to find that the average film thickness was 210nm with a deviation of ±7nm. When a 1μm square area and a 50μm square area of the surface were observed through an

atomic force microscope at 256x256 points of measurement, the root mean square (Rrms) of surface roughness was 10.1nm for the 1μm square areas and 9.8nm for the 50μm square areas. When the boron concentration was measured by means of secondary ion mass spectrography (SIMS), it was found that the boron concentration in the single crystal silicon film was $1.2x10^{18}/cm^3$.

All the obtained SOI wafers were placed on respective SiC trays 31 as shown in FIG. 7 and put into a vertical heat treatment furnace shown in FIG. 9 and comprising a furnace tube made of fused quartz. Gas was made to flow from above to below in the furnace. The wafers were arranged horizontally on the respective SiC trays in such a way that the rear surface of each of the trays supporting an SOI wafer thereon faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available silicon wafer 3 was arranged on a tray, which was then placed on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,000°C and held to that level for 15 hours before the temperature

was lowered to take out the wafers and observe the film thickness of the SOI layer of each specimen again. The decrease in the film thickness of each of the SOI wafers was less than 1nm for all the SOI wafers.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.11nm for a 1μm square area and 0.50nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS) to find that the boron concentration had been reduced to less than $1x10^{16}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices. (Example 10: WJ separation/epitaxial layer transfer/vertical furnace)

For each specimen, the surface of an 8-inch boron-doped Si wafer having a specific resistance of 0.017 Ωcm and a (100) orientation was anodized in a solution containing 49% HF and ethylalcohol mixed to a ratio of 2:1 to produce a 3μm thick porous silicon layer on the wafer surface. To be more accurate, the porous silicon layer included a 2μm thick highly porous layer having a porosity of about 45% and a 1μm thick

26 JUN 2002

lowly porous layer having a porosity of 20% located on the highly porous layer, which layers were produced by varying the electric current. The silicon wafer was then heat-treated at 400°C in an oxygen atmosphere for 1 hour to produce a thin silicon oxide film on the surface of the low porosity porous layer and the wall surfaces of the pores located near that surface. Subsequently, the silicon wafer was dipped into a 1.25% HF aqueous solution for 30 seconds to remove the very thin oxide film formed on the surface of the low porosity porous layer and the wall surfaces of the pores located near that surface. The silicon wafer was then washed well with water and dried. Thereafter, the silicon wafer was placed in an epitaxial growth system and heat-treated at 1,100°C in a hydrogen atmosphere by adding silane gas at a very small rate to shut almost all the pores on the surface of the low porosity porous silicon. Then, a single crystal silicon film was formed on the low porosity porous silicon having shut pores to an average thickness of 310nm±5nm by adding dichlorosilane as silicon source gas to the hydrogen gas. The silicon wafer was then taken out of the epitaxial growth system and placed in an oxidizing furnace. Thus, the surface of the single crystal silicon film was oxidized to produce a 200nm thick silicon oxide film by means of combustion gas of oxygen and hydrogen. As a result of oxidation, the single

26 JUN 2002

crystal silicon film came to show a thickness of 210nm. Meanwhile, a second silicon wafer was subjected to a thermal oxidation process to form a 200nm thick silicon oxide film on the entire surface thereof and each of the wafers was subjected to a wet cleansing operation that is popularly used in a silicon device process to produce a clean surface. Then, the two silicon wafers were bonded together. The silicon wafer assembly obtained by bonding the two wafers was placed in a heat treatment furnace, where it was heat-treated at 1,100°C for 1 hour to enhance the bonding strength at the interface. An atmosphere of a mixture of nitrogen and oxygen was used for the heat treatment. Then, the silicon wafer assembly was separated along the highly porous layer under the fluid wedge effect by applying a high pressure water jet stream a lateral side of the assembly to expose the porous layer on the single crystal silicon film of the second silicon wafer. It was found that the single crystal silicon film had been transferred onto the second silicon wafer with the silicon oxide film to produce an SOI wafer having a residual porous silicon layer. The silicon oxide film on the rear surface of all the obtained SOI wafers having a residual porous silicon layer was etched out in advance by means of hydrofluoric acid and the SOI wafers were put into a vertical heat treatment furnace as shown in FIG. 10. Gas was made to flow from above

26 JUN 2002

to below in the furnace. The wafers were arranged horizontally on a SiC boat as shown in FIG. 9 in such a way that the rear surface of each of the SOI wafers faces the surface of the SOI layer of the SOI wafer located directly below it and the oppositely disposed surfaces are separated by a gap of about 6mm, the center of each of the wafers agreeing with the center line of the furnace tube. A commercially available bulk silicon wafer from which the natural silicon film, if any, had been removed was arranged on top of the SOI wafers, keeping the above pointed out gap to separate it from the top SOI wafer. After replacing the atmosphere in the furnace by hydrogen, the temperature in the furnace was raised to 1,100°C and held to that level for 4 hours before the temperature was lowered to take out the wafers and observe the film thickness of the SOI of each specimen again.

After the heat treatment, the specimens were observed through an atomic force microscope for surface roughness. The root mean square of surface roughness (Rrms) of each of the specimens was 0.12nm for a 1μm square area and 0.34nm for a 50μm square area to indicate that the specimens had been smoothed to the level of commercially available silicon wafers. After the heat treatment, the boron concentration of the single crystal silicon film of each of the specimens was observed by secondary ion mass spectrography (SIMS)

26 JUN 2002

to find that the boron concentration had been reduced to less than $5x10^{15}/cm^3$ to prove that the specimen could feasibly be used for manufacturing electronic devices.

As described above by way of examples, according to the invention, the surface of a semiconductor article having a single crystal silicon film can be smoothed to the level of commercially available silicon wafers, minimizing the reduction in the film thickness of the single crystal silicon film on the surface to practically nil without introducing crystal defects such as a distorted layer that may be produced by an ordinary smoothing operation. In short, with a method and an apparatus according to the invention, the surface of a semiconductor article such as an SOI substrate can be smoothed and the boron concentration of the article can be reduced without damaging the uniform film thickness of each and every wafer.

Additionally, the above pointed out effect of minimizing the reduction ins the film thickness can be ensured when a plurality of semiconductor articles comprising a single crystal silicon film formed on an insulator are collectively processed without increasing deviations in each and among all of the articles. Thus, for example, the surface of a number of SOI substrates can be smoothed and their boron concentration can be reduced collectively, maintaining the uniformity of film thickness.

26 JUN 2002

Still additionally, since the temperature level involved in a method according to the invention is the one that is normally observed in ordinary semiconductor processes, the present invention can be applied to existing semiconductor heat treatment processes for manufacturing semiconductor devices. The heat treatment process to be conducted for a method according to the invention can be used in conjunction with some other appropriate process.

Finally, a method according to the invention can smooth local single crystal regions such as bottom areas of recesses produced on the surface of a semiconductor article as a result of surface treatment that can not be smoothed by ordinary polishing.

26 JUN 2002

WHAT IS CLAIMED IS:

1. A method for heat-treating an SOI substrate having a silicon surface comprising a step of:

heat-treating said SOI substrate in a hydrogen-containing reducing atmosphere, with keeping said SOI substrate in a state disposed opposite to a plane comprising a material comprised of a non-oxidized silicon as a main component with a predetermined distance separating them.

2. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said material is selected from a group consisting of silicon, silicon carbide and silicon nitride.

3. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said silicon surface is an unpolished surface.

4. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said silicon surface has a surface roughness attributable to a porous silicon layer.

5. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said silicon surface has a surface roughness

26 JUN 2002

attributable to micro-cavities.

6. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said SOI substrate has a buried insulation film obtained as a result of oxygen ion implantation and heat treatment.

7. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said plane surface is obtained by removing a natural oxide film.

8. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a plurality of said SOI substrates are arranged so as to have their said respective silicon surfaces arranged in parallel with each other.

9. A method for heat-treating an SOI substrate having a silicon surface according to claim 8, wherein each of said SOI substrates is arranged to face a rear surface of an adjacent SOI substrate from which rear surface any oxide film is removed.

10. A method for heat-treating an SOI substrate having a silicon surface according to claim 8, wherein

26 JUN 2002

any said adjacent SOI substrates are arranged with their silicon surfaces facing each other.

11. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a plurality of SOI substrates are arranged coaxially at predetermined intervals and directed to a same direction; and

a dummy substrate having said plane surface is arranged to face said silicon surface of the leading SOI substrate.

12. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said SOI substrate is placed in a container having an inner wall surface of non-oxidized silicon.

13. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said SOI substrate is placed in a container comprising an outer tube comprised of silicon oxide and an inner tube having an inner surface comprised of non-oxidized silicon.

14. A method for heat-treating an SOI substrate having a silicon surface according to claim 13, wherein hydrogen gas is supplied into said inner tube and

26 JUN 2002

exhausted from said inner tube by way of a flow path between the inner tube and the outer tube.

15. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a plurality of said SOI substrates are supported by a support member having a surface comprising non-silicon oxide so as to be arranged in parallel with each other in a container having an inner wall surface also comprising non-oxidized silicon.

16. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein the root mean square of surface roughness in 1μm square area of said silicon surface is made to be not greater than 0.4nm after the heat treatment.

17. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a plurality of said SOI substrates, each having a silicon surface, are arranged coaxially in parallel with each other at predetermined intervals to face a same direction and a dummy substrate having at least a non-oxidized silicon surface is arranged foremost to face the silicon surface of the leading SOI substrate.

18. A method for heat-treating an SOI substrate

26 JUN 2002

having a silicon surface according to claim 1, wherein said SOI substrate has an Si layer formed by epitaxial growth.

19. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said SOI layer of said SOI substrate has a thickness of not greater than 450nm.

20. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a flow rate of gas running near and in parallel with a principal surface of said SOI substrate is made smaller than a flow rate of gas running perpendicularly relative to a principal surface in an outer peripheral area of the SOI substrate.

21. A method for heat-treating an SOI substrate having a silicon surface according to claim 20, wherein the flow rate of gas running near the principal surface of said SOI substrate is made practically equal to 0.

22. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a silicon oxide film of a rear surface of said SOI substrate is removed to expose the non-oxidized silicon of the rear surface.

26 JUN 2002

23. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a plurality of said SOI substrates are arranged such that each SOI substrate is placed on a tray having a rear surface of non-oxidized silicon with the SOI layer facing upward and vis-a-vis the rear surface of the tray located immediately thereabove.

24. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein a counter-surface constituting member containing silicon carbide as principal ingredient is arranged opposite to the SOI substrate with hydrogen gas interposed therebetween for heat treatment.

25. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein the hydrogen-containing reducing atmosphere substantially contains hydrogen or hydrogen and inert gases.

26. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said hydrogen-containing reducing atmosphere shows a dew point not higher than -92°C.

27. A method for heat-treating an SOI substrate

26 JUN 2002

having a silicon surface according to claim 1, wherein said SOI substrate is supported by a member containing Si, SiC or SiN at least on the surface as principal ingredient.

28. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said SOI substrate is so arranged in the container as to make its principal surface stand perpendicular relative to a main stream of gas introduced into the container.

29. An etching apparatus for carrying out a heat treatment method according to claim 1.

30. An etching apparatus according to claim 29, which comprises a furnace having an inner surface comprising non-oxidized silicon and adapted to contain an SOI substrate and reduce the internal pressure.

31. A method of preparing an SOI substrate, which comprises a steps of:

smoothing a surface of the SOI substrate by a heat treatment method according to claim 1.

32. A method of preparing an SOI substrate, which comprises a step of:

26 JUN 2002

reducing an impurity concentration of an SOI layer of the SOI substrate by a heat treatment method according to claim 1.

33. A method of preparing an SOI substrate having a silicon film, which comprises steps of:

bonding a second article and a first article containing a separation layer for defining a separating position;

transferring said silicon film onto said second article by separating the bonded first and second articles at the layer defining said separating position;

arranging a plane surface of non-silicon oxide opposite to said silicon film transferred onto said second article and heat-treating said silicon film in a hydrogen-containing reducing atmosphere.

34. A method of preparing an SOI substrate having a silicon film, which comprises steps of:

bonding a first article and a second article;

removing a part of said first article from said bonded first and second articles so as to leave a silicon film on said second article; arranging a plane non-oxidized silicon surface opposite to an unpolished surface of said silicon film; and heat-treating said silicon film in a hydrogen-containing reducing

26 JUN 2002

atmosphere.

35. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, further comprising a step of removing a silicon oxide film on the rear surface of said second article.

36. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, further comprising a step of preparing a first article having a non-porous single crystal silicon film formed on a porous silicon layer, bonding the non-porous single crystal silicon film to the second article, and removing said porous silicon prior to an etching step.

37. A method of preparing an SOI substrate having a silicon film according to claim 33, wherein said separation layer is a porous layer and said heat treatment step is conducted after selectively etching the residual porous layer remaining on said silicon film after the separation.

38. A method of preparing an SOI substrate having a silicon film according to claim 33, wherein said separation layer is a porous layer and said heat treatment step is conducted with the residual porous layer remaining on said silicon film after the

26 JUN 2002

separation.

39. A method of preparing an SOI substrate having a silicon film according to claim 33, wherein said separation layer is a layer implanted with inert gas or hydrogen ions and said heat treatment step is conducted without polishing said silicon film surface exposed after the separation.

40. A method of preparing an SOI substrate having a silicon film according to claim 34, wherein said removal step includes a step of removing the residual porous layer remaining on said silicon film.

41. A method of preparing an SOI substrate having a silicon film according to claim 34, wherein the porous layer remains on said silicon film after the removal step.

42. A method of preparing an SOI substrate having a silicon film according to claim 34, wherein the surface of said silicon film is a surface subjected to plasma etching after said removal step.

43. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein said silicon film surface has a root mean square of

26 JUN 2002

surface roughness in 1μm square area of not smaller than 0.2nm.

44. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein a flow rate of gas running near and in parallel with the surface of said SOI substrate is made lower than a flow rate of gas running perpendicularly relative to the surface of the outer peripheral area of the SOI substrate in said heat treatment step.

45. A method of preparing an SOI substrate having a silicon film according to claim 44, wherein the flow rate of gas running near the surface of said SOI substrate is made practically equal to 0.

46. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein said hydrogen-containing reducing atmosphere shows a dew point not higher than -92°C.

47. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein said SOI substrate is supported by a member containing Si, SiC or SiN at least on the surface as principal ingredient.

26 JUN 2002

48. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein said SOI substrate is arranged so as to make its surface disposed perpendicularly relative to the principal flow of gas introduced in a container.

49. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein the silicon oxide film of the rear surface of said SOI substrate is removed to expose the rear surface comprised of the non-oxidized silicon.

50. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein a plurality of SOI substrates are arranged such that each SOI substrate is placed on a tray having a rear surface comprised of non-oxidized silicon with the SOI layer facing upward and vis-a-vis the rear surface of the tray located immediately thereabove.

51. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein a counter-surface constituting member containing silicon carbide as principal ingredient is arranged opposite to the SOI substrate with hydrogen gas interposed therebetween for heat treatment.

26 JUN 2002

52. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein the hydrogen-containing reducing atmosphere substantially contains hydrogen or hydrogen and inert gases.

53. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein the root mean square of surface roughness of said silicon surface is made to be not greater than 0.4nm in a 1μm square area after the heat treatment.

54. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein a plurality of SOI substrates, each having a silicon surface, are arranged coaxially in parallel with each other at predetermined regular intervals to face a same direction and a dummy substrate having at least an non-oxidized silicon surface is arranged foremost to face the silicon surface of the leading SOI substrate.

55. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein said silicon surfae is an SOI layer formed by epitaxial growth.

56. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein

26 JUN 2002

said silicon surface before etching has a thickness of not greater than 450nm.

57. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein said SOI layer of said SOI substrate has a thickness between 20nm and 250nm.

58. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein the temperature of said heat treatment is higher than 300°C and lower than the melting point of silicon.

59. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein the temperature of said heat treatment is higher than 800°C and lower than the melting point of silicon.

60. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein the temperature of said heat treatment is higher than 300°C and lower than the melting point of silicon.

61. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein the temperature of said heat treatment is higher than 800°C and lower than the melting point of silicon.

26 JUN 2002

62. A method of preparing an SOI substrate having a silicon film according to claim 33 or 34, wherein the flow rate of gas flowing along the outer peripheral area of said silicon film article in the furnace is not smaller than 10cc/min•cm^2 and not greater than 300cc/min•cm^2.

63. A method of preparing an SOI substrate having a silicon film according to claim 33, wherein further comprising a step of:

blowing fluid to a lateral surface of the bonded first and second articles to mechanically cleave them.

64. A method of preparing an SOI substrate having a silicon film according to claim 63, wherein said separation layer includes at least a pair of layers having different porosities.

65. A method for heat-treating an SOI substrate having a silicon surface according to claim 19, wherein said SOI layer of said SOI substrate has a thickness between 20nm and 250nm.

66. A method for heat-treating an SOI substrate having a silicon surface according to claim 1, wherein said SOI substrate is transferred to a container without exposing the inside of said container to oxidizing atmosphere.