METHOD FOR FUSING AND FLATTENING BORON-PHOSPHURETED SILICATE GLASS FILM

BACKGROUND OF THE INVENTION

The present invention relates to the improvement of a method for fusing and flattening a boron-phosphureted silicate glass film as an insulating film that is used for a semiconductor device.

Conventionally, a method for fusing and flattening a boron-phosphureted silicate glass film by heat treatment has been used as a method for forming an insulating film in the wiring process of the manufacture of a semiconductor device. Recently, it has been necessary to enhance the flatness of the insulating film in a short time at a low temperature as much as possible with higher integration and step difference of the semiconductor device. It has been known that the boron-phosphureted silicate glass film is fused in a shorter time at a lower temperature if the concentrations of boron and phosphorus contained therein are higher. For this reason, a boron-phosphureted silicate glass film which contains boron and phosphorus having high concentrations has conventionally been used.

As an example of the prior art, a method for fusing and flattening a boron-phosphureted silicate glass film which is used as a method for forming an insulating film in a method for manufacturing a semiconductor device will be described below with reference to sectional views showing the process in Figs.

28 (a) to 28 (c).

First of all, a thermal oxide film is formed over the top face of a silicon substrate 1, and a nitride film is deposited on the thermal oxide film. Then, a photoresist is applied, exposed and developed. A window is formed in a region of a face on which the photoresist is applied where a selective oxide film (LOCOS film) 2 for isolation is to be formed. By using the photoresist as a mask, the nitride film is etched and the thermal oxide film is then etched so that they are removed. Thus, the surface of the silicon substrate 1 is exposed in the region. Thereafter, the photoresist is removed, and the exposed portion of the silicon substrate 1 is oxidized in an oxidizing atmosphere to form the selective oxide film 2 having a thickness of about 500 nm. Subsequently, the nitride film and the thermal oxide film are removed.

As shown in Fig. 28 (a), the surface of the silicon substrate 1 is thermally oxidized to form a gate oxide film 3 having a thickness of 20 nm, for example. Then, a polycrystalline silicon to be a polycrystalline silicon gate layer 4 having a thickness of 400 nm is formed by a CVD (Chemical Vapor Deposition) method, for example. This polycrystalline silicon is doped with impurities in order to reduce a resistance value. As a doping method, a non-doped polycrystalline silicon is formed and impurities are then injected by ion implantation or impurities are diffused from the vapor phase of an impurity gas, and a gas containing an impurity element is mixed with a gas which causes the

polycrystalline silicon to grow by using a CVD device for producing the polycrystalline silicon so as to form the polycrystalline silicon containing the impurities simultaneously with growth.

By using usual photolithography, the polycrystalline silicon is then etched by using, as a mask, the photoresist having the window formed in a predetermined region thereof so that the polycrystalline silicon gate layer 4 is formed. Subsequently, arsenic ions are implanted over the whole face of the silicon substrate 1, and heat treatment is performed for about 30 minutes at a temperature of 900℃ to form a diffusion layer (diffusion layer wiring) 5. In this case, the gate layer 4 and the selective oxide film 2 act as masks and ions are not implanted in portions of the silicon substrate 1 which are located just under the polycrystalline silicon gate layer 4 and the selective oxide film 2. Thus, a MOS type transistor formed by the silicon substrate 1, the gate oxide film 3, the polycrystalline silicon gate 4 and the diffusion layer 5 is completed.

Furthermore, a boron-phosphureted silicate glass film 6 having a boron concentration of 4.5 wt% and a phosphorus concentration of 7.0 wt% is formed as an insulating film on the completed MOS type transistor by a CVD method by using the mixed gas of diborane, phosphine, silane, oxygen and argon (see Fig. 28 (a)).

In order to easily form a wiring on the boron-phosphureted silicate glass film 6, heat treatment is performed for 60

minutes in a nitrogen atmosphere at a temperature of 800 to 950℃ (for example, 900℃) to fuse and flatten the boron-phosphureted silicate glass film 6 as shown in Fig. 28 (b).

As shown in Fig. 28 (c), the boron-phosphureted silicate glass film 6 is etched by using the photoresist as a mask so that a contact hole 7 is formed in a predetermined portion on the diffusion layer (diffusion layer wiring) 5. Then, an aluminum film 8 is formed by sputtering. The aluminum film 8 is etched by using the photoresist as a mask to form an aluminum wiring.

In the fusing and flattening method according to the prior art, however, in the case where the boron-phosphureted silicate glass film 6 is fused and flattened by heat treatment as shown in Fig. 28 (b), boron and phosphorus in the boron-phosphureted silicate glass film 6 are diffused outward to form a sludge such as boron-phosphorus oxide or the like on the surface of the boron-phosphureted silicate glass film 6. The sludge (hereinafter referred to as abnormal particles) affects processing precision with which the aluminum film is processed. Remarkably, the disconnection of the aluminum wirings and the short-circuit between the wirings are caused.

If the boron concentration and the phosphorus concentration of the boron-phosphureted silicate glass film are lowered to reduce the abnormal particles, flatness becomes poorer when performing the fusing and flattening method. Consequently, the processing precision of the wiring is affected so that the disconnection of the wirings and the

short-circuit between the wirings are caused. The poor flatness caused by a reduction in the boron and phosphorus concentrations can be compensated for by increasing a heat treatment temperature or a heat treatment time when performing the fusing and flattening method. However, the diffusion layer 5 excessively extends by the heat treatment so that the characteristics of the MOS type transistor including the diffusion layer 5 are changed.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for fusing and flattening a boron-phosphureted silicate glass film with good flatness while effectively inhibiting or eliminating the generation of abnormal particles.

In order to achieve the above-mentioned object, the present invention employs a structure in which the formation of the abnormal particles that are sludges such as boron-phosphorus oxide and the like can be effectively inhibited during heat treatment for fusing and flattening the boron-phosphureted silicate glass film.

More specifically, the present invention is characterized by a method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate, and heat treating the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon in a heat treating furnace at a temperature of 800 to

950℃ under gas flow having a value of 0.25 (1/min) or more which is obtained by dividing the total gas flow in the heat treating furnace by a tube capacity in the heat treating furnace.

Furthermore, the present invention is characterized in that a boron-phosphureted silicate glass film is formed on the top face of a semiconductor substrate or an insulator substrate, and the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon is heat treated in a heat treating furnace at a temperature of 800 to 950℃ in an atmosphere of the mixed gas of hydrogen and nitrogen.

Moreover, the present invention is characterized in that a boron-phosphureted silicate glass film is formed on the top face of a semiconductor substrate or an insulator substrate, the boron-phosphureted silicate glass film is water-washed, and the semiconductor substrate or insulator substrate having the water-washed boron-phosphureted silicate glass film is heat treated in a heat treating furnace.

In addition, the present invention is characterized in that a boron-phosphureted silicate glass film is formed on the top face of a semiconductor substrate or an insulator substrate, an organic film is applied on the surface of the boron-phosphureted silicate glass film, and the semiconductor substrate or insulator substrate having the organic film applied thereon is heat treated in a heat treating furnace.

Furthermore, the present invention is characterized in

that a boron-phosphureted silicate glass film is formed on the top face of a semiconductor substrate or an insulator substrate, and the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon is heat treated in a heat treating furnace with the inside of the heat treating furnace kept in the pressure reducing condition which is less than an atmospheric pressure.

Moreover, the present invention is characterized in that a boron-phosphureted silicate glass film is formed on the top face of a semiconductor substrate or an insulator substrate, the boron-phosphureted silicate glass film is baked once, and the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film baked thereon is heat treated in a heat treating furnace.

In addition, the present invention is characterized in that a boron-phosphureted silicate glass film is formed on the top face of a semiconductor substrate or an insulator substrate with a boron-phosphorus concentration of a central portion set lower than that of a peripheral portion, and the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon is heat treated in a heat treating furnace.

Furthermore, the present invention is characterized in that boron-phosphureted silicate glass films are formed on the top faces of a plurality of semiconductor substrates or insulator substrates, respectively, the semiconductor substrates or insulator substrates having the boron-

phosphureted silicate glass films formed thereon are located apart from each other with set pitches in a heat treating furnace, and a gas is caused to flow into each space between the semiconductor substrates or insulator substrates in the heat treating furnace to heat treat the semiconductor substrates or insulator substrates having the boron-phosphureted silicate glass films formed thereon.

With the above-mentioned structure according to the present invention, since the speed of the gas which flows in the heat treating furnace is high, the impurity concentration of the gas is lowered in the vicinity of the surface of the boron-phosphureted silicate glass film. Consequently, the reaction of deposition caused by boron and phosphorus of the boron-phosphureted silicate glass film is inhibited or eliminated. Thus, the formation of abnormal particles can be inhibited or eliminated effectively.

According to the present invention, excess boron and phosphorus gases present on the surface of the boron-phosphureted silicate glass film are crystallized to form boron-phosphorus oxide once under the heat treatment in the atmosphere of the mixed gas of hydrogen and nitrogen. However, the boron-phosphorus oxide reacts to a hydrogen gas in the mixed gas to become a boric acid gas and a phosphoric acid gas. Consequently, a sludge such as the boron-phosphorus oxide is not formed.

Furthermore, the excess boron and phosphorus present on the surface of the boron-phosphureted silicate glass film are

washed by water and removed. Consequently, the boron-phosphorus concentration is lowered in the vicinity of the surface of the boron-phosphureted silicate glass film. Accordingly, the formation of the abnormal particles is inhibited or eliminated effectively when performing heat treatment.

In addition, the organic film is formed on the surface of the boron-phosphureted silicate glass film so that the boron-phosphureted silicate glass film does not come in contact with moisture in the air. Consequently, the formation of the abnormal particles is eliminated effectively on the surface of the boron-phosphureted silicate glass film.

According to the present invention, the pressure in the heat treating furnace is kept in the pressure reducing condition during the heat treatment. Consequently, the mean free path of molecules is increased and the impurity concentration of the gas is lowered in the vicinity of the surface of the boron-phosphureted silicate glass film during the heat treatment. Consequently, the formation of the abnormal particles is inhibited or eliminated effectively.

Moreover, the boron-phosphureted silicate glass film is baked. Therefore, water which is adsorbed onto the surface of the boron-phosphureted silicate glass film, a boric acid hydrate, a phosphoric acid hydrate and the like are removed and the impurities in the boron-phosphureted silicate glass film are bonded more strongly. Consequently, the formation of the abnormal particles is inhibited or eliminated effectively.

In addition, the boron-phosphorus concentration of the central portion of the boron-phosphureted silicate glass film is lower than that of the peripheral portion thereof. Consequently, even though the gas flow speed is low in the central portion during the heat treatment, the impurity concentration is reduced in the vicinity of the central portion of the surface of the boron-phosphureted silicate glass film. Consequently, the formation of the abnormal particles is inhibited or eliminated effectively in the central portion.

According to the present invention, a plurality of semiconductor substrates or insulator substrates are provided apart from each other with set pitches in the heat treating furnace. In that condition, a gas flows in the space between the semiconductor substrates or insulator substrates during the heat treatment. Consequently, boron and phosphorus which are diffused outward over the surface of the boron-phosphureted silicate glass film formed on each semiconductor substrate or insulator substrate are removed and discharged efficiently by the gas flow. Thus, the formation of the abnormal particles is inhibited or eliminated effectively.

The above-mentioned object and novel characteristics of the present invention will become more completely apparent from the following detailed description in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings show preferred embodiments of the present invention wherein:

Figures 1 (a) to 1 (f) show the process for manufacturing a semiconductor device according to a first embodiment of the present invention, Figure 1 (a) being a sectional view showing a semiconductor device in which a selective oxide film is formed, Figure 1 (b) being a sectional view showing the semiconductor device in which a polycrystalline silicon gate film is formed, Figure 1 (c) being a sectional view showing the semiconductor device in which a boron-phosphureted silicate glass film is formed, Figure 1 (d) being a sectional view showing the semiconductor device in which the boron-phosphureted silicate glass film is flattened, Figure 1 (e) being a sectional view showing the semiconductor device in which a contact hole is formed, and Figure 1 (f) being a sectional view showing the semiconductor device in which an aluminum wiring is formed;

Figure 2 is a schematically sectional view showing a heat treating furnace which acts as a fusing and flattening device;

Figure 3 is a chart showing the gas substitution speed dependency for the density of abnormal particles generated on a silicon substrate having a diameter of 6 inches;

Figure 4 is a chart showing the gas substitution speed dependency for the density of the abnormal particles generated on a silicon substrate having a diameter of 8 inches;

Figure 5 is a chart showing the hydrogen / nitrogen flow ratio dependency for the density of the abnormal particles;

Figure 6 is a chart showing the ammonia / nitrogen gas

ratio dependency for the density of the abnormal particles;

Figure 7 is a chart showing the washing time dependency of the concentration of phosphorus which is diffused over the surface of the boron-phosphureted silicate glass film;

Figure 8 is a chart showing the washing time dependency for the density of the abnormal particles;

Figure 9 is a chart showing the elapsed time dependency for the density of the abnormal particles which is obtained after washing;

Figure 10 is a sectional view showing a semiconductor device in which an organic film is formed on the surface of a boron-phosphureted silicate glass film according to a sixth embodiment of the present invention;

Figure 11 is a chart showing the time dependency of the density of phosphoric and boric acid hydrates generated on the boron-phosphureted silicate glass film from the formation of the boron-phosphureted silicate glass film to the application of the organic film on the surface of the boron-phosphureted silicate glass film;

Figure 12 is a sectional view showing a semiconductor device in which a boron silicate glass film is formed on the surface of a boron-phosphureted silicate glass film according to a seventh embodiment of the present invention;

Figure 13 is a chart showing the boron silicate glass film thickness dependency for the density of abnormal particles;

Figure 14 is a chart showing the boron silicate glass film thickness dependency for the flattened shape angle of the

boron-phosphureted silicate glass film;

Figure 15 is a sectional view showing a semiconductor device in which a boron-phosphureted silicate glass film having a low boron-phosphorus concentration is formed on the surface of a boron-phosphureted silicate glass film according to an eighth embodiment of the present invention;

Figure 16 is a chart showing the thickness dependency of the boron-phosphureted silicate glass film having a low boron-phosphorus concentration for the density of abnormal particles;

Figure 17 is a chart showing the thickness dependency of the boron-phosphureted silicate glass film having a low boron-phosphorus concentration for the flattened shape angle of the boron-phosphureted silicate glass film;

Figure 18 is a sectional view showing a semiconductor device in which a boron-phosphureted silicate glass film having a high film formation temperature is formed on the surface of a boron-phosphureted silicate glass film according to a ninth embodiment of the present invention;

Figure 19 is a chart showing the relative formation temperature dependency for the density of abnormal particles;

Figure 20 is a sectional view showing a heat treating furnace which acts as a fusing and flattening device according to a tenth embodiment of the present invention;

Figure 21 is a chart showing the pressure dependency in the heat treating furnace for the density of the abnormal particles;

Figure 22 is a chart showing the baking time dependency of

a boron-phosphureted silicate glass film for the density of the abnormal particles;

Figure 23 is a chart showing the distribution of the abnormal particles generated on a silicon substrate in the case where the peripheral and central portions of the boron-phosphureted silicate glass film have the same boron-phosphorus concentration;

Figure 24 is a chart showing the phosphorus concentration gradient dependency in the peripheral and central portions of the boron-phosphureted silicate glass film for the density of the abnormal particles;

Figure 25 is a sectional view showing a heat treating furnace which acts as a fusing and flattening device according to a thirteenth embodiment of the present invention;

Figure 26 is a chart showing the gas substitution speed dependency for the density of abnormal particles according to the thirteenth embodiment of the present invention;

Figure 27 is a chart showing the distribution of the abnormal particles generated on a silicon substrate according to the thirteenth embodiment of the present invention; and

Figures 28 (a) to 28 (c) show the prior art, Figure 28 (a) being a sectional view showing a semiconductor device in which a boron-phosphureted silicate glass film is formed, Figure 28 (b) being a sectional view showing the semiconductor device in which the boron-phosphureted silicate glass film is flattened, and Figure 28 (c) being a sectional view showing the semiconductor device in which an aluminum wiring is formed.

DETAILED DESCRIPTION OF THE INVENTION

Preferred embodiments of the present invention will be described below with reference to the accompanying drawings.

(First Embodiment)

A method for fusing and flattening a boron-phosphureted silicate glass film according to a first embodiment of the present invention will be described below.

Fig. 1 is a sectional view showing the process. In Fig. 1, the reference numeral 11 denotes a silicon substrate (a semiconductor substrate or an insulator substrate), the reference numeral 12 denotes a thermal oxide film, the reference numeral 13 denotes a nitride film, the reference numeral 14 denotes a selective oxide film (LOCOS film), the reference numeral 15 denotes a gate oxide film, the reference numeral 16 denotes a polycrystalline silicon gate film, the reference numeral 17 denotes a diffusion layer (diffusion layer wiring), the reference numeral 18 denotes a boron-phosphureted silicate glass film, the reference numeral 19 denotes a contact hole, and the reference numeral 20 denotes an aluminum film.

Fig. 2 schematically shows a heat treating furnace which is used when fusing and flattening the boron-phosphureted silicate glass film. In Fig. 2, the reference numeral 11 denotes a silicon substrate, the reference numeral 31 denotes a quartz substrate supporting jig, the reference numeral 32 denotes a motor driven door, the reference numeral 33 denotes a quartz reaction pipe, the reference numeral 34 denotes a heater, the reference numeral 35 denotes a gas inlet, and the

reference numeral 36 denotes a gas outlet.

In the following, the process will be described in order. First of all, the thermal oxide film 12 is formed over the top face of the silicon substrate 11 having a diameter of 6 inches in a steam atmosphere at a temperature of 900℃. The nitride film 13 is deposited on the thermal oxide film 12 at a growth temperature of 770℃ by using dichlor-silane and an ammonia gas. Then, a photoresist is applied, exposed and developed. A window is formed in a region of a face on which the photoresist is applied where the selective oxide film (LOCOS film) 14 for isolation is to be formed. By using the photoresist as a mask, the nitride film 13 is etched and the thermal oxide film 12 is etched by a buffer hydrofluoric acid solution so that they are removed. Consequently, the surface of the silicon substrate 11 is exposed in the region. Thereafter, the photoresist is removed, and the exposed portion of the silicon substrate 11 is oxidized in an oxidizing atmosphere to form the selective oxide film 14 having a thickness of about 500 nm. Subsequently, the nitride film 13 is removed by a phosphoric acid solution and the thermal oxide film 12 is removed by the buffer hydrofluoric acid solution. Thus, the top face of the silicon substrate 11 is isolated by the selective oxide film 14 (Fig. 1 (a)).

Thereafter, the surface of the silicon substrate 11 is thermally oxidized in a steam atmosphere at a temperature of 900℃ to form the gate oxide film 15 having a thickness of 20 nm, for example. Then, a polycrystalline silicon to be the

polycrystalline silicon gate layer 16 having a thickness of 400 nm is formed by a CVD method by using a silane gas at a formation temperature of about 610℃, for example. Then, this polycrystalline silicon is doped with impurities in order to reduce a sheet resistance to 30Ω or less.

By usual photolithography, reactive ion etching is performed on the polycrystalline silicon, for example, with the mixed gas of sulfur hexafluoride, hydrogen chloride and oxygen by using, as a mask, the photoresist having the window formed in regions other than the polycrystalline silicon gate layer 16. Thus, the polycrystalline silicon gate layer 16 is formed. Then, arsenic ions are implanted, for example, at an amount of 3×10^{15} / cm^2 over the whole face of the silicon substrate 11, and heat treatment is performed for about 30 minutes at a temperature of 900℃ to form the diffusion layer (diffusion layer wiring) 17. In this case, the gate layer 16 and the selective oxide film 14 act as masks so that ions are not implanted in portions of the silicon substrate 11 which are located just under the polycrystalline silicon gate layer 16 and the selective oxide film 14. Thus, a MOS type transistor is formed (Fig. 1 (b)).

Furthermore, the boron-phosphureted silicate glass film 18 having a boron concentration of 4.5 wt%, a phosphorus concentration of 7.0 wt% and a thickness of 600 nm is formed as an insulating film on the top face of the MOS type transistor by a CVD method with the mixed gas of diborane, phosphine, silane, oxygen and argon (Fig. 1 (c)). While a silane based

boron-phosphureted silicate glass film is used in the present embodiment, it is apparent that a boron-phosphureted silicate glass film which is obtained by the reaction of ozone to TEOS (tetraethyl-ortho-silicate) can also be used.

Subsequently, a plurality of silicon substrates 11 having the boron-phosphureted silicate glass films 18 formed thereon are mounted on the quartz substrate supporting jig 31 shown in Fig. 2. Furthermore, the quartz substrate supporting jig 31 is mounted on the motor driven door 32. The motor driven door 32 causes the quartz substrate supporting jig 31 to be inserted in the quartz reaction pipe 33 by the driving operation of a motor which is not shown. The quartz reaction pipe 33 is heated to 900℃ by the heater 34. In addition, a N2 gas is introduced from the gas inlet 35 at a flow of 12 SLM, for example, and is discharged from the gas outlet 36.

The silicon substrates 11 are inserted in the quartz reaction pipe 33 and are then held for 60 minutes. By this heat treatment, the boron-phosphureted silicate glass film 18 formed on the silicon substrate 11 is fused and flattened (Fig. 1 (d)).

At this time, boron and phosphorus are diffused outward over the surface of the boron-phosphureted silicate glass film 18. An amount of impurities such as boron and phosphorus diffused outward which are taken away by an atmospheric gas (a N2 gas) flowing into the surroundings (a substitution amount) is represented by the following equation in the state of gas laminar flow:

$$F = -D\,(dc / dX) \quad \ldots (1)$$

wherein F is the substitution amount, D is a substitution factor, c is a boron-phosphorus concentration, and X is a distance between the impurities and the boron-phosphureted silicate glass film 18.

As is apparent from the equation (1), the amount F of the impurities substituted by the atmospheric gas is proportional to the concentration gradient of the impurities in the vicinity of the surface of the boron-phosphureted silicate glass film 18. Accordingly, when a gas speed (substitution speed) is high, the impurities which are diffused outward are taken away by the gas flow so that the impurity concentration is lowered in the vicinity of the surface of the boron-phosphureted silicate glass film 18. As a result, the reaction of excess boron and phosphorus, that is, the reaction to generate a sludge is caused with difficulty in the position of the boron-phosphureted silicate glass film 18. Thus, it is hard to form abnormal particles.

Fig. 3 shows the result of investigation of the relationship between the substitution speed of the gas and the density of the abnormal particles which is obtained when heat treating the boron-phosphureted silicate glass film 18. As is apparent from Fig. 3, when the substitution speed, that is, a value obtained by dividing the total gas flow in the heat treating furnace (in more detail, in the quartz reaction pipe 33) by a tube capacity in the heat treating furnace (the capacity of the reaction pipe 33) exceeds 0.25 (1/min), the

density of the abnormal particles is lowered so that the generation of the abnormal particles can be inhibited. While the number of the abnormal particles has been confirmed at a substitution speed of up to 0.50 (1/min) in the present embodiment, it is apparent that inhibition effects can be obtained even though the substitution speed exceeds 0.50 (1/min).

Furthermore, we have obtained the same experimental data for a silicon substrate having a diameter of 8 inches. The result is shown in Fig. 4. With the silicon substrate having a diameter of 8 inches, the gas substitution speed should be increased more than in the case where the silicon substrate having a diameter of 6 inches is heat treated. The reason is that a gas flow speed is decreased in the central portion of the silicon substrate having a diameter of 8 inches during heat treatment so that the impurity concentration is increased more in the vicinity of the silicon substrate. Accordingly, it is necessary to further increase the gas substitution speed to inhibit the abnormal particles on the silicon substrate having a diameter of 8 inches.

Subsequently, the heating of the heater 34 is stopped to cool the quartz reaction pipe 33. After the temperature of the quartz reaction pipe 33 is lowered to 800℃ or less, the silicon substrate 11 is taken out of the quartz reaction pipe 33 by the reverse operation to the insertion of the quartz substrate supporting jig 31 by means of the motor driven door 32.

Then, reactive ion etching is performed on the boron-phosphureted silicate glass film 18 with methane trifluoride and oxygen by using a photoresist as a mask so that a contact hole 19 is formed in predetermined portions on the diffusion layer (diffusion layer wiring) 17. Thus, the contact hole 19 is formed to electrically conduct the diffusion layer 17 of the MOS type transistor on which the insulating film 18 is formed and the wiring provided on the insulating film 18 (Fig. 1 (e)).

For example, the aluminum film 20 is formed by sputtering. By using the photoresist as a mask, the reactive ion etching is performed on the aluminum film 20 with mixed gas of boron chloride, chlorine, methyl chloride, nitrogen and helium to form an aluminum wiring. Thus, the formed MOS type transistor and another MOS type transistor which is isolated therefrom by the selective oxide film 14 are electrically conducted by the aluminum wiring. Consequently, a semiconductor device is completed (Fig. 1 (f)).

(Second Embodiment)

A second embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. More specifically, when a silicon substrate 11 having a boron-phosphureted silicate glass film 18 formed thereon is inserted in a quartz reaction pipe 33 to perform heat treatment to 900℃ by a heater 34, a nitrogen gas and a hydrogen gas are introduced from a gas inlet 35 at flows of 11 SLM and 1.0 SLM, for example, and are

discharged from a gas outlet 36, respectively. Since other methods are the same as in Figs. 1 and 2 according to the first embodiment, illustration will be omitted.

As a result of the heat treatment, the boron-phosphureted silicate glass film 18 formed on the silicon substrate 11 is fused and flattened. In this case, the heat treatment is performed in a hydrogen gas atmosphere. For this reason, even though boron and phosphorus are diffused outward over the surface of the boron-phosphureted silicate glass film 18, they react to a hydrogen gas so that a boric acid gas and a phosphoric acid gas are obtained and discharged from the gas outlet 36. Accordingly, abnormal particles which are sludges such as boron-phosphorus oxide and the like are not formed.

Fig. 5 shows the result of investigation of the relationship between the flow ratio of the nitrogen gas to the hydrogen gas and the number of the abnormal particles obtained when heat treating the boron-phosphureted silicate glass film 18. As is apparent from Fig. 5, if the flow ratio of the hydrogen gas to the nitrogen gas exceeds 6 %, the density of the abnormal particles is lowered so that the generation of the abnormal particles can be inhibited. While the density of the abnormal particles has been confirmed at a flow ratio of up to 9% in the present embodiment, it is apparent that inhibition effects can be obtained even through the flow ratio exceeds 9 %.

(Third Embodiment)

A third embodiment of the present invention will be

described below.

The present embodiment is different from the first embodiment in the following respect. More specifically, when a silicon substrate 11 having a boron-phosphureted silicate glass film 18 formed thereon is inserted in a quartz reaction pipe 33 to perform heat treatment to 900℃, a nitrogen gas and an ammonia gas are introduced from a gas inlet 35 at flows of 7.2 SLM and 4.8 SLM, for example, and are discharged from a gas outlet 36, respectively. Since other methods are the same as in Figs. 1 and 2 according to the first embodiment, illustration will be omitted.

As a result of the heat treatment, the boron-phosphureted silicate glass film 18 formed on the silicon substrate 11 is fused and flattened. In this case, boron and phosphorus are diffused outward over the surface of the boron-phosphureted silicate glass film 18. The boron and phosphorus have molecular structures of B_2O_5 and P_2O_3. However, since the heat treatment is performed in an ammonia gas atmosphere, the boron and phosphorus diffused outward react to a hydrogen group in the gas atmosphere so that $H_3PO_4(H_2O)n$ and $H_3BO_3(H_2O)n$ are obtained. Accordingly, abnormal particles having a molecular structure of boron-phosphorus oxide (BPO_4) are not formed. $H_3PO_4(H_2O)n$ and $H_3BO_3(H_2O)n$ are completely removed by performing washing after the heat treatment. Therefore, after-treatment has no problem.

Fig. 6 shows the result of investigation of the relationship between the ratio of the ammonia gas to the

nitrogen gas and the number of the abnormal particles obtained when heat treating the boron-phosphureted silicate glass film 18. As is apparent from Fig. 6, if the ratio of the ammonia gas to the nitrogen gas exceeds 0.4, the density of the abnormal particles is lowered so that the generation of the abnormal particles can be inhibited. While the density of the abnormal particles has been confirmed at a gas ratio of up to 0.66 in the present embodiment, it is apparent that inhibition effects can be obtained even through the gas ratio exceeds 0.66.

While the nitrogen gas contains the ammonia gas in the present embodiment, the present invention is not restricted to ammonia because the formation of the abnormal particles is inhibited by the reaction of boron and phosphorus to a hydrogen group in the gas atmosphere. Thus, the heat treatment may be performed in the gas atmosphere of a hydrogen compound such as steam, a hydrogen peroxide solution or hydroxylamine.

(Fourth Embodiment)

A fourth embodiment of the present invention will be described below.

In the present embodiment, a nitrogen gas and an ammonia gas are introduced from a gas inlet 35 at flows of 7.2 SLM and 4.8 SLM respectively when heat treating a boron-phosphureted silicate glass film 18 in the same manner as in the first embodiment.

As is apparent from the equation (1), the amount F of the impurities substituted by the atmospheric gas is proportional

to the gradient of a boron-phosphorus concentration in the vicinity of the surface of the boron-phosphureted silicate glass film 18. Accordingly, when the substitution factor D of the gas is high, that is, the gas speed (substitution speed) is high, the impurities which are diffused outward are taken away by the gas flow so that the impurity concentration is lowered in the vicinity of the surface of the boron-phosphureted silicate glass film 18. As a result, the reaction of excess boron and phosphorus, that is, the reaction to generate a sludge is caused with difficulty in the position of the boron-phosphureted silicate glass film 18. Thus, it is hard to form abnormal particles. The present embodiment has the same effects as in Fig. 3.

(Fifth Embodiment)

A fifth embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. More specifically, a boron-phosphureted silicate glass film 18 is formed, and is then washed by ultrapure water before a silicon substrate 11 is heat treated in a quarts reaction pipe 33. By performing this process, boron and phosphorus which are present excessively on the surface of the boron-phosphureted silicate glass film 18 are removed. Since other methods are the same as in Figs. 1 and 2 according to the first embodiment, illustration will be omitted.

Fig. 7 shows the result of measurement of the relationship

between a washing time and the concentration of phosphorus present on the surface of the boron-phosphureted silicate glass film 18. The concentration of phosphorus was measured by using FT-IR (the name of a product : IR-EPOCH) manufactured by Newly Co., Ltd. As is apparent from Fig. 7, if the water-washing time is 15 seconds or more, the phosphorus concentration of the boron-phosphureted silicate glass film 18 is lowered. In respect of the characteristics of a measuring device, the concentration is measured over the whole boron-phosphureted silicate glass film 18. For this reason, it is supposed that the phosphorus concentration is lowered more than the result of measurement shown in Fig. 7 in the vicinity of the surface of the boron-phosphureted silicate glass film 18.

In the present embodiment, consequently, boron and phosphorus are diffused outward over the surface of the boron-phosphureted silicate glass film 18 when heat treating the boron-phosphureted silicate glass film 18 which has been washed by water. However, since the concentrations of boron and phosphorus are low in the vicinity of the surface of the boron-phosphureted silicate glass film 18, the amount of outward diffusion is small. Accordingly, the reaction to generate a sludge by excess boron and phosphorus is not caused on the boron-phosphureted silicate glass film 18 so that abnormal particles are not formed.

Fig. 8 shows the result of investigation of the relationship between the washing time and the density of the abnormal particles. When the washing time is set to 15 seconds

or more, impurities such as excess phosphorus present on the surface of the boron-phosphureted silicate glass film 18 are almost removed. Consequently, it is found that the abnormal particles are not formed. While the investigation was performed at a washing time of up to 30 seconds in the present embodiment, it is apparent that the generation of the abnormal particles can be inhibited even though washing is performed for 30 seconds or more.

Furthermore, Fig. 9 shows the result of investigation of the relationship between a time elapsed after water-washing and the density of the abnormal particles. As is apparent from Fig. 9, when the elapsed time exceeds 48 hours, the generation of the abnormal particles is started. It is supposed that the abnormal particles are generated for the following reason. A boron-phosphorus glass is present in the forms of B_2O_3 and P_2O_3 in the boron-phosphureted silicate glass film 18. If the boron-phosphorus glass is left for a long time, it reacts to moisture in the air or water which remains when performing water-washing treatment and is changed to phosphoric acid and boric acid. Then, the phosphoric acid and the boric acid react to become boron-phosphorus oxide BPO_4. Accordingly, it is necessary to perform heat treatment within 48 hours after water-washing.

(Sixth Embodiment)

A sixth embodiment of the present invention will be described below.

The present embodiment is different from the first

embodiment in the following respect. As shown in Fig. 10, after a boron-phosphureted silicate glass film 18 is formed, an organic film 129 having a thickness of about 0.1μm is applied on the surface of the boron-phosphureted silicate glass film 18. Since other methods are the same as in Fig. 2 according to the first embodiment, illustration will be omitted.

The organic film 129 is a polymer including an alkyl group. Therefore, the boron-phosphureted silicate glass film 18 is covered with the polymer including the alkyl group so that the surface thereof does not come in contact with moisture in the air and impurities such as boron and phosphorus present on the surface of the boron-phosphureted silicate glass film 18 are not diffused outward. Accordingly, even though the boron-phosphureted silicate glass film 18 is then heat treated, abnormal particles are not formed. In addition, the organic film 129 applied on the surface of the boron-phosphureted silicate glass film 18 evaporates and disappears by the heat treatment. Consequently, after-treatment is not affected.

Fig. 11 shows the relationship between a time taken from the formation of the boron-phosphureted silicate glass film 18 to the application of the organic film 129 and an amount of hydrates of phosphoric acid and boric acid generated on the surface of the boron-phosphureted silicate glass film 18. As is apparent from Fig. 11, if 6 hours or more elapse before the organic film 129 is applied, the hydrate of phosphoric acid and boric acid is generated on the surface of the boron-phosphureted silicate glass film 18. When the organic film 129

is applied in such a condition, the fused and flattened shape of the boron-phosphureted silicate glass film 18 is affected. In order not to cause such a bad influence, consequently, it is necessary to limit, to 6 hours or less, the time elapsed before the organic film 129 is applied.

(Seventh Embodiment)

A seventh embodiment of the present invention will be described below.

The present invention is different from the first embodiment in the following respect. As shown in Fig. 12, a boron-phosphureted silicate glass film 18 having a boron concentration of 4.5 wt%, a phosphorus concentration of 7.0 wt% and a thickness of 550 nm is formed, and a boron silicate glass film 158 having a boron concentration of 4.5 wt/% and a phosphorus concentration of 0 wt/% is then formed in a thickness of 50 nm on the surface of the boron-phosphureted silicate glass film 18. Thereafter, the boron-phosphureted silicate glass film 18 and the boron silicate glass film 158 are heat treated. Since other methods are the same as in Fig. 2 according to the first embodiment, illustration will be omitted.

In the present embodiment, consequently, the boron-phosphureted silicate glass film 18 is covered with the boron silicate glass film 158 having a phosphorus concentration of 0 wt%. Therefore, boron and phosphorus are diffused outward from the surface of the boron silicate glass film 158 with low concentrations or are not diffused outward therefrom. Thus,

the reaction to generate a sludge is caused with difficulty during the heat treatment. As a result, it is hard to form abnormal particles.

Fig. 13 shows the result of investigation of the relationship between the thickness of the boron silicate glass film 158 and the density of the abnormal particles. As is apparent from Fig. 13, if the thickness of the boron silicate glass film 158 is set to 20 nm or more, the abnormal particles are not formed. While the thickness of the boron silicate glass film 158 was investigated up to 50 nm in the present embodiment, it is apparent that the formation of the abnormal particles can be inhibited effectively even though the thickness is equal to or more than 50 nm.

Fig. 14 shows the relationship between the thickness of the boron silicate glass film 158 and the flattened shape of the boron-phosphureted silicate glass film 18. In Fig. 14, an axis of ordinate indicates a flattened shape angle. The flattened shape angle is defined as follows. A boron-phosphureted silicate glass film is formed, heat treated, and fused and flattened on the surface of a test pattern which is created by a polysilicon film having a height of 800 nm under the same processing conditions as in the present embodiment. In this case, the flattened shape angle is defined as an angle of inclination to a horizontal line of the boron-phosphureted silicate glass film. As is apparent from Fig. 14, if the thickness of the boron silicate glass film 158 is increased, the fused and flattened shape angle is increased so that

flatness is affected. However, if the film thickness is 20 nm or less, the fused and flattened shape angle is not greatly changed. Accordingly, in the case where the boron silicate glass film 158 should be formed, it is necessary to limit the film thickness to 20 nm or less.

(Eighth Embodiment)

An eighth embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. As shown in Fig. 15, a boron-phosphureted silicate glass film 18 having a boron concentration of 4.5 wt%, a phosphorus concentration of 7.0 wt% and a thickness of 550 nm is formed, and another boron-phosphureted silicate glass film 188 having a boron concentration of 3.8 wt% and a phosphorus concentration of 4.5 wt%, that is, the boron-phosphureted silicate glass film 188 having a boron-phosphorus concentration which is about two-thirds or less of that of the bulk boron-phosphureted silicate glass film 18 is then formed in a thickness of 50 nm on the surface of the boron-phosphureted silicate glass film 18. Thereafter, these boron-phosphureted silicate glass films 18 and 188 are heat treated. Since other methods are the same as in Fig. 2 according to the first embodiment, illustration will be omitted.

In the present embodiment, consequently, the ordinary boron-phosphureted silicate glass film 18 is covered with the boron-phosphureted silicate glass film 188 having a low boron-

phosphorus concentration. Therefore, boron and phosphorus are diffused outward from the surface of the boron-phosphureted silicate glass film 188 with low concentrations or are not diffused outward therefrom. Thus, the reaction to generate a sludge is caused with difficulty during the heat treatment. As a result, it is hard to form abnormal particles.

Fig. 16 shows the result of investigation of the relationship between the thickness of the boron-phosphureted silicate glass film 188 having a low boron-phosphorus concentration and the density of the abnormal particles. As is apparent from Fig. 16, if the thickness of the boron-phosphureted silicate glass film 188 is set to 20 nm or more, the abnormal particles are not formed. While the thickness of the boron-phosphureted silicate glass film 188 was investigated up to 50 nm in the present embodiment, it is apparent that the formation of the abnormal particles can be inhibited effectively even though the thickness is equal to or more than 50 nm.

Fig. 17 shows the relationship between the thickness of the boron-phosphureted silicate glass film 188 and the flattened shape of the boron-phosphureted silicate glass film 18. In Fig. 17, an axis of ordinate indicates a flattened shape angle. The flattened shape angle has been defined in the seventh embodiment. As is apparent from Fig. 17, if the thickness of the boron-phosphureted silicate glass film 188 is increased, the fused and flattened shape is affected. However, if the film thickness is 50 nm or less, the fused and flattened

shape is not greatly changed. Accordingly, in the case where the boron-phosphureted silicate glass film 188 having a low boron-phosphorus concentration should be formed, it is necessary to limit the film thickness to 50 nm or less.

(Ninth Embodiment)

A ninth embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. As shown in Fig. 18, a boron-phosphureted silicate glass film 18 having a boron concentration of 4.5 wt%, a phosphorus concentration of 7.0 wt% and a thickness of 550 nm is formed, and a boron-phosphureted silicate glass film 198 which is formed at a film formation temperature that is higher than that of the boron-phosphureted silicate glass film 18 by 20℃ is then formed in a thickness of 50 nm on the surface of the boron-phosphureted silicate glass film 18. Thereafter, these boron-phosphureted silicate glass films 18 and 198 are heat treated. Since other methods are the same as in Fig. 2 according to the first embodiment, illustration will be omitted.

In the present embodiment, consequently, the boron-phosphureted silicate glass film 198 which is formed at a film formation temperature that is higher than an ordinary film formation temperature by 20℃ is more stable than the boron-phosphureted silicate glass film 18 which is formed at the ordinary film formation temperature. The inside (a bulk film) of the ordinary boron-phosphureted silicate glass film 18 is

covered with the boron-phosphureted silicate glass film 198 which is formed at the higher film formation temperature. Therefore, boron and phosphorus are diffused outward from the surface of the boron-phosphureted silicate glass film 198 with low concentrations or are not diffused outward therefrom. Thus, the reaction to generate a sludge is caused with difficulty during the heat treatment. As a result, it is hard to form abnormal particles.

Fig. 19 shows the result of investigation of the relationship between a relative formation temperature and the density of the abnormal particles. The relative formation temperature is defined as a difference between the formation temperature of the boron-phosphureted silicate glass film 198 on a surface layer portion and that of the bulk boron-phosphureted silicate glass film 18. As is apparent from Fig. 19, if the relative formation temperature is 20℃ or more, the abnormal particles are not formed. While the relative formation temperature was investigated up to 20℃ in the present embodiment, it is apparent that the formation of the abnormal particles can also be inhibited effectively at a relative formation temperature of 20℃ or more. The thickness of the boron-phosphureted silicate glass film 198 formed on the surface layer portion at a relative formation temperature of 20℃ was set to 50 nm during experimental investigation. It is supposed that the density of the abnormal particles is increased if the thickness of the boron-phosphureted silicate glass film 198 is reduced. Accordingly, it is desirable that

the boron-phosphureted silicate glass film 198 formed on the surface layer portion should have a thickness of 50 nm or more at present.

(Tenth Embodiment)

A tenth embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following two respects. More specifically, when inserting a silicon substrate 11 having a boron-phosphureted silicate glass film 18 formed thereon in a quartz reaction pipe 33 to perform heat treatment to 900℃, the pressure of the quartz reaction pipe 33 is reduced by a vacuum pump 200 which is provided on the rear end of a gas outlet 36 and heat treatment is performed in this condition as shown in Fig. 20. In addition, when taking the silicon substrate 11 having the boron-phosphureted silicate glass film 18 fused and flattened out of the quartz reaction pipe 33 after the heat treatment, the pressure of the quartz reaction pipe 3 is returned to an atmospheric pressure in advance. In Fig. 20, the reference numeral 201 designates a control valve provided on the gas outlet 36 for adjusting the pressure of the quartz reaction pipe 33 to a set pressure. Since other methods are the same as in Figs. 1 and 2 according to the first embodiment, illustration will be omitted.

As is apparent from the equation (1) for calculating the amount F of the impurities substituted by the atmospheric gas which has been described in the first embodiment, the amount F

of substitution is proportional to the gradient of a boron-phosphorus concentration in the vicinity of the surface of the boron-phosphureted silicate glass film 18. Under the condition that the pressure of the quartz reaction pipe 33 is lower than the atmospheric pressure, accordingly, the concentration of impurities is reduced in the vicinity of the surface of the boron-phosphureted silicate glass film 18 and the reaction to generate a sludge by excess boron and phosphorus on the boron-phosphureted silicate glass film 18 is not caused so that abnormal particles are not formed.

Fig. 21 shows the result of investigation of the relationship between the pressure of the quartz reaction pipe 33 and the density of the abnormal particles which is obtained when heat treating the boron-phosphureted silicate glass film 18. As is apparent from Fig. 21, when a pipe pressure is lower than 300 mTorr, the density of the abnormal particles is extremely lowered so that the generation of the abnormal particles is eliminated. While the number of the abnormal particles has been confirmed at a pipe pressure of up to 100 mTorr in the present embodiment, it is apparent that inhibition effects can be strikingly obtained even though the pipe pressure is lower than 100 mTorr.

(Eleventh Embodiment)

An eleventh embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. More specifically, a

boron-phosphureted silicate glass film 18 is formed and is then put on a hot plate to perform baking treatment at a temperature of 420℃, and a silicon substrate 11 which has been baked is heat treated in a quartz reaction pipe 33. Since other methods are the same as in Figs. 1 and 2 according to the first embodiment, illustration will be omitted.

In the present embodiment, the boron-phosphureted silicate glass film 18 is baked so that water adsorbed onto the surface of the boron-phosphureted silicate glass film 18 evaporates and disappears, or boric acid and phosphoric acid evaporate and disappear, and the bonding of B_2O_3 and P_2O_5 in the boron-phosphureted silicate glass film 18 becomes much more strongly. Accordingly, the concentrations of boron and phosphorus which are diffused outward from the surface of the boron-phosphureted silicate glass film 18 are low during subsequent heat treatment. Consequently, the reaction to generate a sludge is caused with difficulty so that it is hard to form abnormal particles.

Fig. 22 shows the result of investigation of the relationship between a time for baking the boron-phosphureted silicate glass film 18 and the density of the abnormal particles. As is apparent from Fig. 22, if the baking time exceeds 30 seconds, the density of the abnormal particles is extremely reduced so that the generation of the abnormal particles can be eliminated.

The baking temperature should be higher than a temperature at which the boron-phosphureted silicate glass film 18 is

formed by a CVD method. In the present embodiment, if the baking temperature is lower than 420℃, the inhibition effects of the generation of the abnormal particles are reduced. Accordingly, the baking temperature should be 420℃ or more to obtain good effects.

(Twelfth Embodiment)

A twelfth embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. When forming a boron-phosphureted silicate glass film 18, a boron-phosphorus concentration of a central portion is set lower than that of a peripheral portion to form the film, and heat treatment is then performed. A method for changing the boron-phosphorus concentration in the peripheral and central portions of the boron-phosphureted silicate glass film 18 is as follows. More specifically, the boron-phosphorus concentration of the boron-phosphureted silicate glass film 18 is determined by the in-plane temperature distribution of a silicon substrate 11 obtained when forming the film. Therefore, the temperature gradient between the peripheral and central portions of the silicon substrate 11 which is obtained during the formation of the boron-phosphureted silicate glass film 18 is changed. Since other methods are the same as in Figs. 1 and 2 according to the first embodiment, illustration will be omitted.

Fig. 23 shows the distribution of the generation of abnormal particles obtained when forming a boron-phosphureted

silicate glass film having the same boron-phosphorus concentration in the central and peripheral portions. Fig. 23 shows the result of investigation of foreign matter defects having a size of 0.2μm or more by using KLA2130 which is a pattern foreign matter defect inspecting device manufactured by KLA Co., Ltd. In Fig. 23, portions drawn by black points are foreign matter defects. As is apparent from Fig. 23, the foreign matter defects are generated in the central portion of the silicon substrate. The reason is as follows. In the equation (1) for calculating the amount F of the impurities substituted by the atmospheric gas which has been described in the first embodiment, the amount F of substitution is proportional to the gradient of a boron-phosphorus concentration in the vicinity of the surface of the boron-phosphureted silicate glass film 18. However, the speed of a gas which flows from a gas inlet 35 is high in the peripheral portion of a reaction pipe 33 and is low in the central portion thereof. Thus, the gas does not flow smoothly in the central portion of the silicon substrate 11. As a result, the boron-phosphorus concentration is higher in the vicinity of the surface of the boron-phosphureted silicate glass film 18 in the central portion of the silicon substrate 11 than in the peripheral portion thereof. Thus, abnormal particles are generated in the central portion of the silicon substrate 11.

In the present embodiment, however, the boron-phosphorus concentration is lower in the central portion of the boron-phosphureted silicate glass film 18 than in the peripheral

portion thereof. Consequently, even though the gas flow introduced from the gas inlet 35 is not smooth in the central portion of the silicon substrate 11 during heat treatment, it is hard to generate the abnormal particles in the central portion of the boron-phosphureted silicate glass film 18.

Fig. 24 shows the relationship of a phosphorus concentration gradient between the peripheral and central portions of the boron-phosphureted silicate glass film 18 with the density of the abnormal particles. If the phosphorus concentration gradient is 0.5 wt%/mm or less, the abnormal particles having a distribution shown in Fig. 23 are generated in the central portion of the silicon substrate 11. Accordingly, it is desirable that the phosphorus concentration gradient should be set to 0.5 wt%/mm or more to reduce the concentration of impurities in the vicinity of the surface of the central portion of the boron-phosphureted silicate glass film 18. In the present embodiment, if a temperature gradient between the peripheral and central portions of the silicon substrate 11 is set to about -0.3℃/mm, the phosphorus concentration gradient is 0.5 wt%/mm or more.

(Thirteenth Embodiment)

A thirteenth embodiment of the present invention will be described below.

The present embodiment is different from the first embodiment in the following respect. When heat treating a boron-phosphureted silicate glass film 18 in a heat treating furnace, a gas is introduced into a quartz reaction pipe 33

much more properly and the introduced gas causes excess boron and phosphorus present on the surface of the boron-phosphureted silicate glass film 18 to be removed and discharged efficiently.

As shown in Fig. 25, a plurality of silicon substrates 11 are vertically mounted apart from each other with set pitches. For example, the set pitch is 3/16 inch on a silicon substrate having a diameter of 6 inches. The gas is introduced from a gas inlet 35 into the quartz reaction pipe 33 of the heat treating furnace through a gas introducing pipe 210. The gas introducing pipe 210 extends vertically close to the silicon substrates 11 on the sides thereof, and the vertical length of the gas introducing pipe 210 is set to a piping length that is equal to or more than the total length of the maximum number of silicon substrates 11 which can be housed in the reaction pipe 33 of the heat treating furnace in the state where they are vertically mounted apart from each other with the set pitches. As is enlarged in Fig. 25, the gas introducing pipe 210 has a gas blow-off port 212 opened in a portion located on each space between the silicon substrates 11 opposite thereto. A N2 gas is introduced, for example, at a flow of 9 SLM from the gas introducing pipe 210 into the reaction pipe 33. Since other methods are the same as in Fig. 1 according to the first embodiment, illustration will be omitted.

In the present embodiment, accordingly, the gas is blown off from each gas blow-off port 212 of the gas introducing pipe 210, flows transversely in the space between the silicon

substrates 11 and is then discharged from the gas outlet 36 to the outside when heat treating the silicon substrates 11 having the boron-phosphureted silicate glass films 18 formed thereon in the heat treating furnace. As a result, excess boron and phosphorus which are diffused over the surface of the boron-phosphureted silicate glass film 18 of each silicon substrate 11 are removed and discharged effectively by the gas flow. Therefore, it is hard to generate abnormal particles. Fig. 27 shows the result of investigation of the distribution of the abnormal particles generated on the silicon substrate 11 under the above-mentioned conditions. As is apparent from Fig. 27, the abnormal particles are generated very rarely.

Fig. 26 shows the result of investigation of the relationship between a gas substitution speed and the density of the abnormal particles in the present embodiment. As is apparent from Fig. 26, if the gas substitution speed exceeds 0.15 (1/min), the density of the abnormal particles is reduced extremely so that the generation of the abnormal particles can be inhibited effectively. While the number of the abnormal particles has been confirmed at a gas substitution speed of up to 0.40 (1/min) in the present embodiment, it is apparent that the generation of the abnormal particles can be inhibited effectively even though the gas substitution speed exceeds 0.40 (1/min).

According to the present embodiment, the excess boron and phosphorus present on the surface of the boron-phosphureted silicate glass film 18 are substituted and discharged

effectively by the gas flow in the space between the silicon substrates 11. Consequently, the generation of the abnormal particles can be inhibited effectively even though the silicon substrate has a great diameter, for example, a diameter of 8 inches or more.

Although the present invention has fully been described by way of example with reference to the accompanying drawings, it is to be understood that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the invention, they should be construed as being included therein.

WE CLAIM:

1. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate; and

heat treating the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon in a heat treating furnace at a temperature of 800 to 950℃ under gas flow having a value of 0.25 (1/min) or more which is obtained by dividing the total gas flow in the heat treating furnace by a tube capacity in the heat treating furnace.

2. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate; and

heat treating the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon in a heat treating furnace at a temperature of 800 to 950℃ in an atmosphere of the mixed gas of hydrogen and nitrogen.

3. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 2, wherein the mixed gas of hydrogen and nitrogen has the flow ratio of hydrogen to nitrogen which exceeds 6 %.

4. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate; and

heat treating the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon in a heat treating furnace at a temperature of 800 to 950℃ in the gas atmosphere of ammonia or a hydrogen compound such as steam, a hydrogen peroxide solution or hydroxylamine.

5. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 4, wherein the a gas atmosphere is an atmosphere of the mixed gas containing nitrogen in addition to ammonia or a hydrogen compound.

6. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 5, wherein the gas ratio of ammonia to nitrogen exceeds 0.4.

7. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate;

water-washing the boron-phosphureted silicate glass film; and

heat treating the semiconductor substrate or insulator substrate having the water-washed boron-phosphureted silicate

glass film in a heat treating furnace.

8. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 7, wherein a time for water-washing the boron-phosphureted silicate glass film exceeds 15 seconds.

9. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 7 or 8, wherein a time taken from the water-washing of the boron-phosphureted silicate glass film to the start of heat treatment in the teat treating furnace is 48 hours or less.

10. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate;

applying an organic film on the surface of the boron-phosphureted silicate glass film; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having the organic film applied thereon.

11. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 10, wherein a time taken from the formation of the boron-phosphureted silicate glass film to the application of the organic film is 6 hours or less.

12. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate;

forming a boron silicate glass film having no phosphorus implanted therein on the top face of the boron-phosphureted silicate glass film; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having the boron silicate glass film formed thereon.

13. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 12, wherein the thickness of the boron silicate glass film is within a tolerance by which the boron-phosphureted silicate glass film is fused and flattened without a bad influence.

14. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 12 or 13, wherein the thickness of the boron silicate glass film is equal to or less than 50 nm.

15. . A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate;

forming, on the top face of the boron-phosphureted silicate glass film, a boron-phosphureted silicate glass film having each implantation amount of boron and phosphorus set low; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having two kinds of the boron-phosphureted silicate glass films formed thereon.

16. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 15, wherein the thickness of the boron-phosphureted silicate glass film having each implantation amount of boron and phosphorus set low is within a tolerance by which a bulk boron-phosphureted silicate glass film is fused and flattened without a bad influence.

17. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 16, wherein the thickness of the boron-phosphureted silicate glass film having each implantation amount of boron and phosphorus set low is equal to or less than 50 nm.

18. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 15, wherein the boron-phosphorus concentration of the boron-phosphureted silicate glass film having each implantation amount of boron and phosphorus set low is within a tolerance by which the bulk boron-phosphureted silicate glass film is fused and flattened without a bad influence.

19. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 18, wherein the boron-phosphorus concentration of the boron-phosphureted silicate glass film having each implantation amount of boron and phosphorus set low is equal to or less than about two-thirds of the boron-phosphorus concentration of the bulk boron-

phosphureted silicate glass film.

20. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate;

forming another boron-phosphureted silicate glass film on the top face of the boron-phosphureted silicate glass film at a formation temperature which is higher than the formation temperature of the boron-phosphureted silicate glass film by 20℃ or more; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having two kinds of the boron-phosphureted silicate glass films formed thereon.

21. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 20, wherein the thickness of another boron-phosphureted silicate glass film formed on the top face of the boron-phosphureted silicate glass film is equal to or less than 50 nm.

22. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon with the

inside of the heat treating furnace kept in the pressure reducing condition which is less than an atmospheric pressure.

23. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 22, wherein the temperature of the heat treating furnace is set to a temperature which is equal to or more than 800℃ and equal to or less than 950℃ to perform heat treatment in the heat treating furnace with the pressure of the heat treating furnace kept in the pressure reducing condition which is equal to or less than 760 mTorr.

24. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate;

baking the boron-phosphureted silicate glass film once; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film baked thereon.

25. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 24, wherein a baking temperature is equal to or more than 420℃.

26. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 24, wherein a baking time is equal to or more than 30 seconds.

27. A method for fusing and flattening a boron-

phosphureted silicate glass film, comprising the steps of:

forming a boron-phosphureted silicate glass film on the top face of a semiconductor substrate or an insulator substrate with a boron-phosphorus concentration of a central portion set lower than that of a peripheral portion; and

heat treating, in a heat treating furnace, the semiconductor substrate or insulator substrate having the boron-phosphureted silicate glass film formed thereon.

28. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 27, wherein the gradient of the boron-phosphorus concentration between the central and peripheral portions of the boron-phosphureted silicate glass film is equal to or less than 0.5 wt%/mm.

29. A method for fusing and flattening a boron-phosphureted silicate glass film, comprising the steps of:

forming boron-phosphureted silicate glass films on the top faces of a plurality of semiconductor substrates or insulator substrates, respectively;

locating, in a heat treating furnace, the semiconductor substrates or insulator substrates having the boron-phosphureted silicate glass films formed thereon apart from each other with set pitches; and

causing a gas to flow into each space between the semiconductor substrates or insulator substrates in the heat treating furnace to heat treat the semiconductor substrates or insulator substrates having the boron-phosphureted silicate glass films formed thereon.

30. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 29, wherein the gas which flows into the heat treating furnace is supplied from a gas introducing pipe having a piping length which is equal to or more than the total length of the maximum number of semiconductor substrates or insulator substrates which can be housed in the heat treating furnace apart from each other with set pitches.

31. The method for fusing and flattening a boron-phosphureted silicate glass film of Claim 29, wherein the amount of the gas which flows into the heat treating furnace has a value of 0.15 or more which is obtained by dividing the total gas flow in the heat treating furnace by a tube capacity of the heating treating furnace.