

DESCRIPTION

METHOD OF USING BORON DIFFUSION SOURCE AND METHOD FOR PRODUCING
SEMICONDUCTOR

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TECHNICAL FIELD

The present invention relates to a method of using a boron diffusion source and a method for producing a semiconductor using the boron diffusion source.

10 BACKGROUND ART

In order to form p-type semiconductors by diffusing boron on a semiconductor wafer made of e.g. germanium or silicon, it has been common that a boron diffusion source and a semiconductor wafer are placed in a furnace (for example, they are alternatively arranged at regular intervals) and heated in a non-oxidizing gas atmosphere. In such a case, as the diffusion progresses, since boron oxide in the boron diffusion source is consumed, it gradually tends to be difficult to uniformly diffuse boron. Therefore, a treatment to reoxidize the boron diffusion source is carried out at a suitable timing to form boron oxide on the surface has been carried out, however, time and cost are required for such reoxidizing treatment (Patent Document 1).

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Patent Document 1: JP-A-2006-294964

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DISCLOSURE OF THE INVENTION

OBJECT TO BE ACCOMPLISHED BY THE INVENTION

It is an object of the present invention to provide a method of using a boron diffusion source, whereby time until carrying out the reoxidizing treatment can be extended, and a method for producing a semiconductor using such a boron diffusion source.

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MEANS TO ACCOMPLISH THE OBJECT

The present inventors have extensively studied to accomplish the above object, and as a result, they have achieved an invention having the following constructions, whereby the above object has been accomplished.

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(1) A method of using a boron diffusion source, characterized by using a boron diffusion source made of a composite sintered body comprising an alumina (Al_2O_3) component, a silica (SiO_2)

component and a boron nitride (BN) component in a non-oxidizing gas atmosphere with an oxygen concentration of from 0.3 to 5 vol%.

(2) The method of using a boron diffusion source according to the above (1), wherein the non-oxidizing gas is supplied to a diffusion furnace at a rate of from 0.5 to 15L/min.

5 (3) The method of using a boron diffusion source according to the above (1) or (2), wherein as the boron diffusion source, a composite sintered body is used wherein the total content of the alumina (Al_2O_3) component and the silica (SiO_2) component is from 30 to 70 mass%, the content of the boron nitride (BN) component is from 30 to 70 mass%, and the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is from 1.0 to 2.4.

10 (4) The method of using a boron diffusion source according to any one of the above (1) to (3), wherein the alumina (Al_2O_3) starting material is γ -alumina or α -alumina.

(5) The method of using a boron diffusion source according to any one of the above (1) to (3), wherein the silica (SiO_2) starting material is silica powder, aerosil or borosilicate glass.

(6) The method of using a boron diffusion source according to any one of the above (1) to (3),
15 wherein the boron nitride (BN) starting material is boron nitride powder.

(7) The method of using a boron diffusion source according to any one of the above (1) to (6), wherein the boron diffusion source has an open porosity of from 10 to 45% as measured by Archimedes' method.

(8) A method for producing a semiconductor, characterized by placing a boron diffusion source
20 made of a composite sintered body comprising an alumina (Al_2O_3) component, a silica (SiO_2) component and a boron nitride (BN) component wherein as the boron diffusion source, a composite sintered body is used wherein the total content of the alumina (Al_2O_3) component and the silica (SiO_2) component is from 30 to 70 mass%, the content of the boron nitride (BN) component is from 30 to 70 mass%, and the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is from 1.0 to 2.4, and a semiconductor wafer in a
25 diffusion furnace and heating them under a non-oxidizing gas atmosphere having an oxygen concentration of from 0.3 to 5 vol%.

(9) The method for producing a semiconductor according to the above (8), wherein the non-oxidizing gas is supplied to a diffusion furnace at a rate of from 0.5 to 15L/min.

30 EFFECTS OF THE INVENTION

According to the present invention, time until carrying out the reoxidizing treatment can be extended, since boron oxide is always present on the surface of the boron diffusion source. Further,

it is possible to provide a method for producing a semiconductor which is preferably used for producing p-type semiconductors by diffusing boron on a semiconductor wafer.

BEST MODE FOR CARRYING OUT THE INVENTION

5 In the present invention, from 0.3 to 5 vol% of oxygen is contained in the non-oxidizing atmosphere so that boron oxide to be consumed by diffusion is continuously supplied at such a rate that the boron diffusion is not impaired. If the oxygen concentration is less than 0.3 vol%, the amount of boron oxide formed on the surface of the boron diffusion source is insufficient, and therefore reoxidation has to be carried out frequently. On the other hand, if the oxygen
10 concentration exceeds 5 vol%, both the boron diffusion source and the semiconductor wafer are excessively oxidized, and the amount of boron diffusion in the inside of a semiconductor wafer may be reduced. The oxygen concentration in the non-oxidizing atmosphere is preferably from 0.5 to 3.5 vol%, more preferably from 0.8 to 2.5 vol%.

The oxygen concentration in the non-oxidizing atmosphere can be measured, for example, by
15 a galvanic cell type measuring apparatus (tradename "standard type oxygen monitor OXYMAN", manufactured by Taiei Denki).

As a material of the semiconductor wafer, germanium or silicon may, for example, be used.

The non-oxidizing atmosphere of the present invention may, for example, be an atmosphere of nitrogen, hydrogen, argon, helium, neon or a mixture thereof. Among them, nitrogen gas is
20 preferred. The non-oxidizing atmosphere with an oxygen concentration of from 0.3 to 5 vol% can be maintained in the diffusion furnace, for example, by supplying a carrier gas prepared so as to have such a composition to the diffusion furnace at a rate of from 0.5 to 15 L (liter)/min.

As the diffusion furnace, a horizontal or vertical type furnace provided with means to control the diffusion temperature and the flow rate of carrier gas may be used. As a specific example,
25 "Model 272-M400", tradename, manufactured by Koyo Thermo Techno may be mentioned. One example of the rate of raising temperature, temperature and retention time at the time of diffusion is shown in Examples.

In a case where, as in the present invention, the boron diffusion source is a composite sintered body comprising an alumina (Al_2O_3) component, a silica (SiO_2) component and a boron
30 nitride (BN) component, a part of boron oxide (boric acid anhydride) formed by oxidation of boron nitride becomes aluminum borate having a high melting point. Therefore, even if the diffusion temperature is as high as 950°C or higher, adhesion between jigs and boron source and falling (flow

down) of boron oxide can be reduced. Further, alumina and silica in the composite sintered body exist mainly in the form of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, whereby the mechanical strength of the boron diffusion source is also improved.

In the boron diffusion source of the present invention, the content of the boron nitride component is preferably from 30 to 70 mass%, the total content of the alumina (Al_2O_3) component and the silica (SiO_2) component is preferably from 30 to 70 mass%, and the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is preferably from 1.0 to 2.4. If the content of the boron nitride (BN) component is less than 30 mass%, since the amount of boron oxide formed at the time of diffusion is less, it is difficult to uniformly diffuse boron, and if it exceeds 70 mass%, the amount of boron oxide formed is excessive, whereby boron oxide excessively attaches on the surface of a semiconductor wafer, and deposition on jigs or the like tends to be large. The content of boron nitride (BN) component is particularly preferably from 35 to 65 mass%, and the total content of the alumina (Al_2O_3) component and the silica (SiO_2) component is particularly preferably from 35 to 65 mass%.

Further, if the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is less than 1.0, the effect to extend time until the reoxidation treatment becomes small. For the same reason, the open porosity of the boron diffusion source measured by the Archimedes' method is preferably at least 10%. On the other hand, if the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ exceeds 2.4, since deformation of the boron diffusion source at the time of diffusion is large, it is difficult to diffuse boron uniformly. For the same reason, the open porosity of the boron diffusion source measured by the Archimedes' method is preferably at most 45%. The molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is particularly preferably from 1.2 to 2.0, and the porosity of the boron diffusion source is particularly preferably from 15 to 30%.

The composite sintered body made of the boron diffusion source of the present invention comprising an alumina (Al_2O_3) component, a silica (SiO_2) component and a boron nitride (BN) component can be produced by preparing a mixed material having the above composition and hot press sintering it or CIP molding (Cold Isostatic Press) it, followed by sintering in a non-oxidizing atmosphere such as nitrogen or argon.

As a raw material containing an alumina (Al_2O_3) component, γ -alumina or α -alumina which preferably has an average particle size of from 0.02 to 5 μm may, for example, be used.

Further, as a raw material containing a silica (SiO_2) component, silica powder, aerosol or glass borate which preferably has an average particle size of from 0.02 to 5 μm may, for example, be used. The material containing both an alumina (Al_2O_3) component and a silica (SiO_2) component may, for example, be mullite.

As a material containing a boron nitride (BN) component, commercially available boron nitride powder having an average particle size of preferably from 0.1 to 30 μm may be simply used.

The hot press sintering conditions may, for example, be such that the pressure is preferably from 5 to 15 MPa, more preferably from 6 to 12 MPa, the temperature is preferably from 1,400 to 1,800°C, more preferably from 1,420 to 1,700°C, and the time is from 1 to 10 hours, preferably from 2 to 8 hours.

The CIP molding condition may, for example, be such that the molding pressure is preferably from 100 to 500 MPa, more preferably from 300 to 500 MPa. The conditions for sintering a CIP molded product may, for example, be such that the temperature is preferably from 1,500 to 1,900°C, more preferably from 1,600 to 1,800°C, and the time is preferably from 1 to 10 hours, more preferably from 2 to 8 hours.

An obtained composite sintered body is mechanically processed into a disk shape or a plate shape by a lathe, fraise, slicing machine or the like.

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples. However, the present invention is by no means restricted to such specific Examples.

EXAMPLES 1 to 12 and COMPARATIVE EXAMPLES 1 to 6

Boron nitride powder (BN purity: at least 99 mass%, average particle size: 7 μm), alumina powder (Al_2O_3 purity: at least 99 mass%, average particle size: 0.2 μm) and borosilicate glass powder (purity: at least 99 mass%, composition: 90 mass% of SiO_2 component and 10 mass% of B_2O_3 component, average particle size: 2.1 μm) were blended in a ratio shown in Table 1, and mixed by a ball mill for 3 hours. An obtained mixed material was packed in a graphite mold having an inner diameter of 150 mm and hot press sintered at 1,500°C under a pressure of from 8 to 12 MPa in a nitrogen gas atmosphere for 4 hours.

Further, the above mixed material was CIP molded (molded product size: outer diameter of about 150 mm and height of about 60 mm) by using a rubber mold under a pressure shown in Table 1 and sintered under normal pressure at 1,700°C in a nitrogen gas atmosphere for 4 hours.

Respective sintered bodies obtained by the above sintering method were machined into a disk shape (diameter: 125 mm, thickness: 1.5 mm) by a lathe or slicing machine to produce boron diffusion sources, and the porosity, the amount of deformation and the diffusion life time (duration until a reoxidizing treatment is required) were measured by the following methods. The results are shown in Table 1. Further, in the case of the hot pressing, the porosity was controlled by the

sintering pressure, and in the case of pressureless sintering, the porosity was controlled by pressure in CIPing.

(1) Porosity: The porosity was obtained by the following formula in accordance with JIS R1634.

5 Porosity (%) = (water saturated mass – dried mass) × 100/(water saturated mass – mass in water)

(2) Amount of deformation: The boron diffusion source was heated in air at 1,150°C for 10 hours, and then the deformation was measured by a thickness gauge.

(3) Diffusion life time: The boron diffusion source was heated in an oxygen atmosphere at
10 1,100°C for 1.5 hours. Then, the boron diffusion source and a silicon wafer were placed to face each other with a space of 3.5 mm, and while supplying at a rate of 2L/min a carrier gas obtained by variously changing the proportions of nitrogen gas and oxygen gas so that the oxygen concentration in the nitrogen atmosphere in the diffusion furnace became as shown in Table 1, the diffusion test of which one cycle was 1 hour at 1,050°C was repeated. On every cycle, the sheet resistance of the
15 silicon wafer was measured by 4 probe method, and the accumulation time until the sheet resistance value increased at least 20% from the initial value was measured.

TABLE 1

	Sintering method	Blended proportion		Porosity (%)	Degree of deformation (mm)	Oxygen concentration in non-oxidizing gas atmosphere	Diffusion possible time (h)
		BN (mass%)	Al ₂ O ₃ /SiO ₂ molar ratio				
Example 1	Hot press sintering	40	1.6	15	0.2	0.3	420
Example 2	Hot press sintering	40	1.6	15	0.2	0.5	600<
Example 3	Hot press sintering	40	1.6	15	0.2	3.5	600<
Example 4	Hot press sintering	40	1.6	15	0.2	4.5	580
Example 5	Hot press sintering	40	1.6	15	0.2	2	600<
Example 6	Hot press sintering	60	1.6	16	0.3	2	600<
Example 7	Hot press sintering	40	1.6	11	0.1	2	286
Example 8	Hot press sintering	40	1.6	17	0.2	2	600<
	CIP molding (pressure: 500 MPa) followed by pressureless sintering						
Example 9	CIP molding (pressure: 300 MPa) followed by pressureless sintering	40	1.6	22	0.3	2	600<
Example 10	CIP molding (pressure: 100 MPa) followed by pressureless sintering	40	1.6	35	0.5	2	600<
Example 11	Hot press sintering	40	1.2	16	0.3	2	260
Example 12	Hot press sintering	40	2.1	15	0.4	2	600<
Comp. Ex. 1	Hot press sintering	40	1.6	15	0.2	0.2	85
Comp. Ex. 2	Hot press sintering	40	1.6	15	0.2	7	0
Comp. Ex. 3	Hot press sintering	10	1.6	16	0.3	0.2	40
Comp. Ex. 4	Hot press sintering	90	1.6	16	(Attached on a quartz jig at the time of oxygen treatment)		
Comp. Ex. 5	Hot press sintering	40	2.8	15	3.1	(Not measured due to large deformation)	
Comp. Ex. 6	Hot press sintering	40	0.7	16	0.4	0.2	86

From the results of Table 1, it is evident that the diffusion life time until carrying out the reoxidation treatment was substantially extended in Examples, while in Comparative Examples, this effect could not be obtained.

5 INDUSTRIAL APPLICABILITY

The present invention can be used for producing p⁺n connected or p⁺p connected devices for semiconductors production such as solar batteries, inverters, diodes or transistors.

The entire disclosure of Japanese Patent Application No. 2006-321304 filed on November 29,
10 2006 including specification, claims and summary is incorporated herein by reference in its entirety.

What is claimed is:

1. A method of using boron diffusion source, characterized by using a boron diffusion source made of a composite sintered body comprising an alumina (Al_2O_3) component, a silica (SiO_2) component and a boron nitride (BN) component in a non-oxidizing gas atmosphere with an oxygen concentration of from 0.3 to 5 vol%.
2. The method of using boron diffusion source according to Claim 1, wherein the non-oxidizing gas is supplied to a diffusion furnace at a rate of from 0.5 to 15 L/min.
3. The method of using boron diffusion source according to claim 1, wherein as the boron diffusion source, a composite sintered body is used wherein the total content of the alumina (Al_2O_3) component and the silica (SiO_2) component is from 30 to 70 mass%, the content of the boron nitride (BN) component is from 30 to 70 mass%, and the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is from 1.0 to 2.4.
4. The method of using boron diffusion source according to any one of claims 1 to 3, wherein the alumina (Al_2O_3) component is γ -alumina or α -alumina.
5. The method of using boron diffusion source according to any one of claims 1 to 3, wherein the silica (SiO_2) component is silica powder, aerosil or borosilicate glass.
6. The method of using boron diffusion source according to any one of claims 1 to 3, wherein the boron nitride (BN) component is boron nitride powder.

7. The method of using boron diffusion source according to any one of claims 1 to 3, wherein the boron diffusion source having an open porosity of from 10 to 45% as measured by Archimedes' method is used.

8. A method for producing semiconductor, characterized by placing a boron diffusion source made of a composite sintered body comprising an alumina (Al_2O_3) component, a silica (SiO_2) component and a boron nitride (BN) component wherein as the boron diffusion source, a composite sintered body is used wherein the total content of the alumina (Al_2O_3) component and the silica (SiO_2) component is from 30 to 70 mass%, the content of the boron nitride (BN) component is from 30 to 70 mass%, and the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is from 1.0 to 2.4 and a semiconductor wafer in a diffusion furnace and heating them under a non-oxidizing gas atmosphere having an oxygen concentration of from 0.3 to 5 vol.%.

9. The method for producing a semiconductor according to claim 8, wherein the non-oxidizing gas is supplied to a diffusion furnace at a rate of from 0.5 to 15 L/min.