METHOD OF MANUFACTURING A SILICON DIOXIDE LAYER

The invention relates to a method of manufacturing a silicon dioxide layer of low roughness deposited on a substrate and to a method of manufacturing a composite substrate or wafer including such silicon dioxide layer as buried layer, in particular for applications in the fields of optics, optoelectronics or electronics.

The joined figures 1A to 1E illustrate the different steps of a prior art process employed for manufacturing such a composite substrate.

As can be seen on figure 1A, a silicon dioxide layer 2 is firstly deposited on a bulk substrate 1 termed the "source substrate", because it is used to provide the material that will constitute later the top layer of the composite substrate. In view of the kind of composite substrate aimed to be obtained, such source substrate may be, for example, silicon, silicon germanium, strained silicon or germanium.

Among the different techniques used to realize the deposition of the silicon dioxide layer 2, one is known to the skilled person under the acronym "LPCVD TEOS" which means "Low Pressure Chemical Vapour Deposition" of silicon oxide films using "tetraethylorthosilicate" as the source material.

Such deposition is carried out by introducing a substrate or a batch of substrates 1 inside a LPCVD reactor and by exposing the substrates in the reactor to tetraethylorthosilicate, the chemical formula of which is $Si(OC_2H_5)_4$, as the source material for silicon oxide (SiO_2).

This process provides certain advantages in terms of uniformity or density of the oxide layer obtained as compared to other oxide deposition process such as low temperature or high temperature deposition processes.

Then, the dioxide layer 2 thus obtained is submitted to a thermal annealing, in order to improve its structural and electrical properties.

However, layers deposited with TEOS have a significantly higher surface roughness than thermally grown layers. Consequently, an additional chemical mechanical polishing (CMP) step is required to smooth the free surface of the silicon dioxide layer 2, before bonding it with another substrate.

To do so, one uses a polishing head 4 (as can be seen on figure 1B) with an abrasive paste or liquid.

Then, as can be seen in figure 1C, a zone of weakness 10 is created inside the source substrate 1 by implanting atomic species.

The term "atomic species implantation" means any bombardment of molecular or ionic, atomic species which is capable of introducing said species into the material of the source substrate 1, with a maximum concentration of said species located at a given depth from the bombarded surface which depth in the present case is preferably larger than the thickness of the silicon dioxide layer 2. The molecular, ionic or atomic species are introduced into the material with an energy that is also distributed about a maximum.

Implantation of atomic species into said source substrate 1 can be carried out, for example, using an ion beam implanter or a plasma implanter.

Preferably, said implantation is carried out by ionic bombardment. More preferably, the implanted ionic species is hydrogen. Other ionic species can advantageously be used alone or in combination with hydrogen, such as ions of rare gases (for example helium).

The zone of weakness 10 marks the boundary between two portions, namely a thin top layer 11 and the remainder 12 of the substrate.

By way of example, reference can be made to the literature concerning the method known under the trade name "Smart Cut".

A support substrate 3 is then bonded by molecular bonding to the free surface of the silicon dioxide layer 2 (see figure 1D).

Finally, as can be seen on figure 1E, the remainder 12 is detached from the source substrate 1, along the zone of weakness 10, to keep only the top layer 11 on the silicon dioxide layer 2 and the support substrate 3.

Concerning the detachment, one of the following techniques can be used, either alone or in combination: application of stresses of mechanical or electrical origin, chemical etching or supplying energy (laser, microwaves, inductive heating, and furnace treatment). Said detachment techniques are known to the skilled person and will not be described here in more detail.

The composite substrate thus obtained is referenced 4.

In the above-mentioned process, the polishing step of figure 1B presents numerous drawbacks such as the lack of uniformity of the resulting layer 2, the lack of reproducibility of the process and the low throughput of the process.

Further, this additional step increases the manufacturing cost of each substrate or wafer.

The aim of the present invention is to overcome the above-mentioned drawbacks and in particular to delete the step of chemical and mechanical polishing.

Consequently, the invention aims to improve the LPCVD TEOS deposition process, in order to obtain a high quality silicon dioxide layer 2 which meets substrate direct bonding criteria in terms of surface roughness, uniformity and particle density and which can be used as buried oxide layer.

Finally, the invention also aimed to provide an interface with superior electrical features.

To this end, the invention provides a method of manufacturing a silicon dioxide layer of low roughness.

This method is characterized in that it comprises the following steps consisting in:

- depositing a layer of silicon dioxide over a substrate by a low pressure chemical vapour deposition (LPCVD) process, the deposition process employing simultaneously a flow of tetraethylorthosilicate (TEOS) as the source material for the film deposition and a flow of a diluent gas that is not reactive with TEOS, so that the diluant gas / TEOS ratio is between 0.5 and 100;
- annealing said silicon dioxide layer at a temperature between 600°C and 1200°C, for a duration between 10 minutes and 6 hours.

Preferably, the diluant gas is choosen among nitrogen, argon (Ar), helium (He) and a mixture thereof.

Preferably, the annealing is performed at a temperature between 700 °C and 900 °C, for a duration between 1 and 4 hours.

Advantageously, it is carried out in an inert ambient comprising nitrogen, argon or helium or any mixture thereof.

The following other advantageous but non-limiting characteristics of the invention may be taken alone or in combination:

- the nitrogen / TEOS ratio during the deposition process is preferably between 2 and 10, more preferably about 3.6;
- the deposition temperature is preferably between 625°C and 725°C, more preferably between 650°C and 700°C, most preferably about 675°C;
- the deposition pressure is preferably between 10 and 1000 Pa, more preferably between 50 and 150 Pa, most preferably about 100 Pa;

- the TEOS flow is preferably between 10 and 200 sccm, more preferably between 50 and 90 sccm, most preferably about 70 sccm, and the nitrogen flow is preferably between 10 and 2000 sccm, more preferably between 100 and 500 sccm and most preferably about 250 sccm.

Advantageously, an oxygen flow is added to the nitrogen / TEOS mixture, the oxygen flow being between 5 and 100 sccm, preferably between 10 and 40 sccm, and more preferably about 25 sccm.

Preferably, the thickness of said silicon dioxide layer is between 10 and 400 nm.

The invention also provides a method of manufacturing a composite substrate with a buried silicon dioxide layer, in particular for applications in the fields of optics, optoelectronics or electronics.

This method comprises the following steps consisting in :

a) depositing a silicon dioxide layer, on a first substrate termed the "source substrate", by the method according to any preceding claims,

b) implanting atomic species within said source substrate, to define therein a zone of weakness which demarcates a thin top layer from the remainder of said substrate, said thin top layer being in contact with said silicon dioxide layer,

c) directly bonding a second substrate termed the "support substrate" against the silicon dioxide layer, by molecular adhesion,

d) detaching the remainder of the source substrate, along said zone of weakness, in order to obtain said composite substrate.

Advantageously, the source substrate is made of a material selected from silicon, germanium, silicon germanium (SiGe) or strained silicon.

Other characteristics and advantages of the invention become apparent from the following description of the invention.

This description is made with reference to the accompanying drawings in which:

- Figures 1A to 1E are diagrammatic representations of the different steps employed in the prior art method of manufacturing a composite substrate with a buried silicon dioxide layer,

- Figure 2 is a graph showing the standard deviation of silicon dioxide layer thickness (SDT) as a function of the mean thickness value (MT) of the silicon dioxide layer,this latter being deposited according to various "LPCVD TEOS" processes, some of them corresponding to the invention and other to comparative processes.

- Figure 3 is a graph showing the roughness (R) of the silicon dioxide layer as a function of the mean thickness value (MT) of the silicon dioxide layer, this latter being deposited according to various "LPCVD TEOS" processes, some of them corresponding to the invention and other to comparative processes.

According to the invention, the silicon dioxide deposition step of figure 1A is improved as under-mentioned.

The inventors have now discovered that the roughness of a silicon dioxide layer obtained by a "LPCVD TEOS" deposition process may be lowered by the use of a flow of a diluent gas, simultaneously with a flow of TEOS during the deposition process. The diluent gas is preferably nitrogen but it can be any other gas that is not reactive with TEOS, of which argon (Ar) and helium (He) are non-limiting examples. Alternatively, any mixture of such non-reactive gases can be used.

The trials to determine the best operating conditions will now be described.

Silicon dioxide deposition was performed by a low pressure vapour chemical deposition (LPVCD) process, which consists in:

- introducing a batch of source substrates inside the process chamber of a LPCVD reactor,
- introducing gaseous flow of different chemical reactants, at elevated temperature, under low pressure, in order to form silicon dioxide layer as a result of chemical reaction between gaseous reactants.

The reactor used in these trials was a vertical batch reactor, known under the trade mark of "A400", sold by the company ASM.

The gaseous reactants were tetraethylorthosilicate (TEOS), oxygen, and in some cases nitrogen.

TEOS is a relatively inert material, liquid at room temperature. TEOS vapour can be supplied to the process chamber of the reactor either from a bubbler using a carrier gas such as nitrogen or argon, or from a direct liquid injection system.

1) Comparative processes.

a) process A.

Three silicon dioxide layers have been manufactured respectively on three silicon substrates using the operating conditions mentioned below in Table 1.

Table 1.

Step name	Time (hh:mm:ss)	Temp (°C)	N_2-flow (sccm)	TEOS flow (sccm)	O_2 flow (sccm)	Pressure (MTorr)
Boat in	0:10:00	650	1000	-	-	atm
Pump	0:15:30	to 675	-	-	-	-
Purge	0:10:30	675	500	-	-	750
Pump/Leakcheck	0:07:20	675	-	-	-	-
Stabilize	0:30:00	675	500	-	-	750
Pre-deposition	0:05:00	675	-	-	100	-
Deposition	0:48:30	675	-	70	25	750
Post-deposition	0:05:00	675	-	-	100	
Pump/Purge	0:15:00	675	500	-	-	-
Backfill	0:11:00	to 650	5000	-	-	to atm
Boat out	0:10:00	650	-	-	-	atm

"atm" means "atmospheric pressure".

"sccm" means "standard cubic centimeters per minute".

750 m Torr is equivalent to 100 Pa.

The silicon dioxide layer is formed by the following chemical reaction:

$$Si(OC_2H_5)_4 \text{ (liquid)} \rightarrow SiO_2 \text{ (solid)} + 4C_2H_4 \text{ (gas)} + 2H_2O \text{ (gas)}$$

In this case, nitrogen is only used to purge the process chamber but is not present during the deposition step.

The deposition process has been repeated in order to obtain silicon dioxide layers of different thicknesses..

This process is referred to as process A.

b) Process B.

Process A has been repeated using the operating conditions mentioned in Table 1, except that the deposition pressure was of 1200 m Torr (160 Pa) instead of 750 mTorr (100 Pa).

This process is referred to as process B.

c) Process C.

Process A has been repeated using the operating conditions mentioned in Table 1, except that the deposition temperature was of 635°C instead of 675°C, and that the TEOS flow was 50 sccm instead of 70 sccm.

This process is referred to as process C.

2) Processes according to the invention.

a) Process D.

The above-mentioned process has been repeated but with the operating conditions mentioned below in Table 2.

Table 2.

Step name	Time (hh:mm:ss)	Temp (°C)	N_2-flow (sccm)	TEOS flow (sccm)	O_2 flow (sccm)	Pressure (MTorr)
Boat in	0:10:00	650	1000	-	-	atm
Pump	0:15:30	to 675	-	-	-	-
Purge	0:10:30	675	500	-	-	750
Pump/Leakcheck	0:07:20	675	-	-	-	-
Stabilize	0:30:00	675	500	-	-	750
Pre-deposition	0:05:00	675	500	-	100	-
Deposition	0:49:00	675	500	70	25	750
Post-deposition	0:05:00	675	500	-	100	
Pump/Purge	0:15:00	675	500	-	-	-
Backfill	0:11:00	to 650	5000	-	-	to atm
Boat out	0:10:00	650	-	-	-	atm

"atm" means "atmospheric pressure".

"sccm" means "standard cubic centimeters per minute".

750 m Torr is equivalent to 100 Pa.

This process is referred to as process D.

b) Process E.

Process D has been repeated but with a nitrogen flow of 250 sccm instead of 500 sccm.

This process is referred to as process E.

The main deposition parameters of the five above-mentioned processes are summarized below in Table 3.

Table 3. Comparison of TEOS deposition steps.

Process name	Temp (°C)	TEOS flow (sccm)	N2 flow (sccm)	O2 flow (sccm)	Pressure (Pa)	N_2/TEOS Ratio
Process A	675	70	0	25	100	0
Process B	675	70	0	25	160	0
Process C	635	50	0	25	100	0
Process D	675	70	500	25	100	7.2
Process E	675	70	250	25	100	3.6

Then, the different silicon dioxide layers have been submitted to an annealing step, in nitrogen or argon, at atmospheric pressure, at a temperature between 700 and 900°C, during 1 to 4 hours.

After densification of the silicon dioxide (SiO_2) layer obtained by the annealing step, the thickness of this SiO_2 layer has been measured by an ADE ACUMAP reflectometer.

The results are shown on figure 2.

The graph of figure 2 represents the standard deviation of thickness (SDT) in angstroms (0.1 nm) of the SiO_2 layer after densification, versus the mean thickness after deposition (MT) in angstroms (0.1 nm), for the SiO_2 layers obtained by processes A to E.

As can be seen on said figure, good results in term of thickness uniformity are obtained with process D and better results are obtained with process E, in particular for thicknesses below 200 nm.

Further, roughness measurements were performed by AFM technique for 1 x 1 μm^2 scan in the center of the different densified oxide layers.

The results are shown on figure 3.

The graph of figure 3 represents the roughness RMS value (R) in angstroms (0.1 nm) versus the mean thickness after deposition (MT) in angstroms (0.1 nm), for the SiO_2 layers obtained by processes A to E.

The aim of such roughness measurements is obviously to characterize the ability of the oxide layer to be directly bonded to the support substrate.

The bonding is typically allowed by roughness below 0,55 nm.

As can be seen on figure 3, the thicker the deposition is, the rougher it is. Nevertheless, at a given thickness, process E gives the best results, i.e. the low roughness.

Additionally, a plasma activation treatment of one or both of the surface(s) to be bonded may be achieved in order to further enhanced bonding energy.

Finally, the best operating conditions according to the process of the invention can be summarized as follows:

TEOS: preferably between 10 and 200 sccm, more preferably between 50 and 90 sccm, most preferably about 70 sccm.

Oxygen flow: preferably between 5 and 100 sccm, more preferably between 10 and 40 sccm, most preferably about 25 sccm.

Nitrogen flow: preferably between 10 and 2000 sccm, more preferably between 100 and 500 sccm, most preferably about 250 sccm,

Ratio of nitrogen:tetraethylorthosilicate: preferably between 0.5 and 100, more preferably between 2 and 10, most preferably around 3.6.

Deposition temperature: preferably between 625°C and 725°C, more preferably between 650°C and 700°C, most preferably about 675°C.

Deposition pressure: preferably between 10 and 1000 Pa, more preferably between 50 and 150 Pa, most preferably about 100 Pa.

Annealing conditions : preferably a temperature between 600°C and 1200°C, for a duration between 10 minutes and 6 hours, more preferably a temperature between 700 and 900°C, for a duration between 1 and 4 hours.

Although the anneal is most simply carried out in an anneal furnace operating at atmospheric pressure, the anneal can also be carried out at a lower or higher pressure. Operating conditions within the range define above are dependant on specific deposition reactor conditions, as for instance reactor geometry and dimensions.

Further the anneal ambient appeared not to be very critical. Although inert anneal ambients such as nitrogen, argon or helium have the advantage that the substrate under the deposited oxide layer is not oxidized , it appeared that both anneals in an inert ambient, as well as anneals in oxidizing ambient such as air, or nitrogen / air mixtures, reduced the surface roughness of the films.

It will be clear that in a manufacturing process an inert anneal ambient is preferred as oxidation of the underlying substrate during the anneal is undesirable.

The invention also provides a method of manufacturing a composite substrate 4, as previously described with reference to figures 1A to 1E but in which the step of LPCVD is realized according to the above described process.

Further, the CMP prior art step of figure 1B is deleted.

By way of example, substrates known under the acronym "SOI", "SGOI", "sSOI" and "GOI" which mean respectively "silicon on insulator", "silicon germanium on insulator", "strained silicon on insulator" and "germanium on insulator" can thus be obtained, by using respectively silicon, silicon germanium, strained silicon and germanium as source substrate 1.

CLAIMS

1. A method of manufacturing a silicon dioxide layer (2) of low roughness, comprising the step of:

- depositing a layer of silicon dioxide (2) over a substrate (1) by a low pressure chemical vapour deposition (LPCVD) process, the deposition process employing simultaneously a flow of tetraethylorthosilicate (TEOS) as the source material for the film deposition and a flow of a diluant gas that is not reactive with TEOS, so that the diluant gas / TEOS ratio is between 0.5 and 100;

- annealing said silicon dioxide layer at a temperature between 600°C and 1200°C, for a duration between 10 minutes and 6 hours.

2. The method of claim 1 wherein the diluent gas is choosen among nitrogen, argon (Ar), helium (He) and a mixture thereof.

3. The method of claim 1 or 2 wherein the annealing is performed at a temperature between 700 °C and 900 °C, for a duration between 1 and 4 hours.

4. The method of any preceding claims wherein the annealing is carried out in an inert ambient comprising nitrogen, argon or helium or any mixture thereof.

5. The method of any preceding claims wherein the nitrogen / TEOS ratio during the deposition process is between 2 and 10.

6. The method of claim 5 wherein the nitrogen / TEOS ratio during the deposition process is about 3.6.

7. The method of any preceding claims wherein the deposition temperature is between 625°C and 725°C.

8. The method of claim 7 wherein the deposition temperature is between 650°C and 700°C.

9. The method of claim 8 wherein the deposition temperature is about 675°C.

10. The method of any preceding claims wherein the deposition pressure is between 10 and 1000 Pa.

11. The method of claim 10 wherein the deposition pressure is between 50 and 150 Pa.

12. The method of claim 11 wherein the deposition pressure is about 100 Pa.

13. The method of any preceding claims wherein the TEOS flow is between 10 and 200 sccm and the nitrogen flow is between 10 and 2000 sccm.

14. The method of claim 13 wherein the TEOS flow is between 50 and 90 sccm and the nitrogen flow is between 100 and 500 sccm.

15. The method of claim 14 wherein the TEOS flow is about 70 sccm and the nitrogen flow is about 250 sccm.

16. The method of any preceding claims wherein an oxygen flow is added to the nitrogen / TEOS mixture, the oxygen flow being between 5 and 100 sccm.

17. The method of claim 16 wherein the oxygen flow is between 10 and 40 sccm.

18. The method of claim 17 wherein the oxygen flow is about 25 sccm.

19. The method according to anyone of the preceding claims wherein the thickness of said silicon dioxide layer (2) is between 10 and 400 nm.

20. A method of manufacturing a composite substrate (4) with a buried silicon dioxide layer (2), in particular for applications in the fields of optics, optoelectronics or electronics, characterized in that it comprises the following steps consisting in :

- a) depositing a silicon dioxide layer (2), on a first substrate (1) termed the "source substrate", by the method according to any preceding claims,
- b) implanting atomic species within said source substrate (1), to define therein a zone of weakness (10) which demarcates a thin top layer (11) from the remainder (12) of said substrate, said thin top layer (11) being in contact with said silicon dioxide layer (2),
- c) directly bonding a second substrate (3) termed the "support substrate" against the silicon dioxide layer (2), by molecular adhesion,
- d) detaching the remainder (12) of the source substrate (1), along said zone of weakness (10), in order to obtain said composite substrate (4).

21. The method according to claim 20 wherein source substrate (1) is comprising material selected from silicon, germanium, silicon germanium (SiGe) or strained silicon.