A METHOD OF PRODUCING A STRUCTURE COMPRISING AT LEAST ONE SUPPORT SUBSTRATE AND AN ULTRATHIN LAYER

The present invention relates to a method of producing a structure comprising at least one support substrate and an ultrathin layer of a material, in particular a semiconductor one, optionally with an interposed layer between them.

During the fabrication of composite substrates, in particular for applications in the fields of optics, electronics, or optoelectronics, layer transfer methods are employed to transfer a layer from a source substrate onto a support substrate.

One of those layer transfer methods consists in implanting atomic species beneath the surface of a source substrate to create therein a zone of weakness which defines a thin layer. The free face of that thin layer is then brought into intimate contact with the support substrate and said thin layer is then detached from the remainder of the source substrate to transfer it to the support substrate.

That type of method is known under the trade mark "Smart Cut".

Technology is moving in the direction of transferring thinner and thinner layers onto a support to obtain composite substrates from which electronic components can be fabricated which function even faster than existing components.

Reference should be made in this regard to the article by Aaron Mand, "Value-Added Wafers Push Chips Ahead", Semiconductor International, November 2002.

However, trials have until now shown that when the thin layer to be transferred is very thin, i.e., less than about 100 nanometers (nm), it contains defects which do not appear when transferring a thicker layer. Thus, it will not withstand subsequent heat treatments carried out either to strengthen its bonding interface with the support or to detach it from the source substrate. Said

heat treatments result in increasing the pressure existing in gas microbubbles present in the zone of weakness and cause them to degas. The very thin transferred layer thus contains many defects such as blisters or partial delamination.

Further, it appears that when a very thin layer is transferred onto a support substrate, the quality of the bond obtained is far more sensitive to the presence of particles or hydrocarbons on the surface of the layers to be brought into contact than when transferring a thicker layer.

Similarly, when an interposed layer is present between the thin layer to be transferred and the support substrate, it has been shown that the thinner the transferred thin layer, the more defects it contains.

Figure 1 of the accompanying drawings shows a theoretical plot of the total thickness ET of the transferred layer, i.e. the sum of the thicknesses of the thin layer and the interposed layer, as a function of the number of defects ND in the finished structure for a given thickness of interposed layer..

This figure, which is for illustrative purposes only, shows that for a given thickness of interposed layer (solid line) there is a limiting thickness EL_1 for the transferred thin layer; smaller values will result in the transfer of a layer containing defects. For a smaller thickness of interposed layer (dotted line), the limiting thickness EL_2 for the transferred thin layer is larger.

In the particular case of silicon on insulator (SOI) substrates, atomic species are implanted, generally hydrogen ions at the surface of a silicon substrate the outer surface of which has been oxidized, then a second silicon substrate is bonded onto the assembly. After detaching and annealing, the SOI substrate comprising a layer of bulk silicon covered with a layer of oxide (SiO_2) and a layer of transferred silicon is obtained (see the

article "Silicon on insulator material technology" by M. Bruel, *Electron Letter*, 31, 1201 (1995)).

Below a certain thickness for the buried oxide layer, it has been shown that the transferred silicon layer contains defects, which are more marked if a high temperature heat treatment is also used. Reference should be made in this regard to the article by Q.-Y. Tong, G. Cha, R. Gafiteau, and U. Gösele, "Low temperature wafer direct bonding", J. Microelectromech Syst, 3, 29 (1994).

One possible explanation for the appearance of said defects is the occurrence of degassing at the bonding interface between the layer of silicon oxide and the second silicon substrate.

During the annealing heat treatment termed "stabilization treatment", which takes place after the detachment step, a gas is formed at the bonding interface. In the case of a thick SOI substrate, the transferred layer is thick and acts as a stiffener. Further, it is assumed that the oxide layer, which is also thick, acts as a sponge, absorbing the gas released from the bonding interface.

In the case of a thin SOI substrate in which the transferred layer and/or oxide layer is/are thin, said phenomena of absorption and of the stiffening effect do not occur and degassing results in poor adhesion at the bonding interface.

A further possible explanation is that in thin SOI substrates, hydrogen is implanted at a shallow depth with respect to the bonding interface. The transferred layer is thus saturated with hydrogen, which tends to migrate by diffusion in the direction of the bonding interface.

SOI substrates obtained using current techniques comprise buried oxide layers (SiO_2) and superficial silicon with thicknesses that are between 100 nm and 1.5 micrometers (μm). Until now, it has been difficult to

obtain good quality SOI substrates in which said two layers are thinner.

Trials carried out up to now in this regard have been aimed at strengthening the bond between the layers without, however, achieving satisfactory results.

Finally, a method for forming an optical silicon layer is known from the document WO-00/48278, said method comprising steps of transferring layer and thinning. This method aims to obtain an optical silicon layer of a specified thickness, named "optical thickness", equal to $\lambda/4n_s$, where λ is the wavelength of the produced or received light and n_s the refractive index of silicon.

However, this method does not aim to obtain an ultrathin layer and consequently does absolutely not mention the problems of appearance of blisters or defects, during the transfer of an ultrathin layer onto a support.

Finally, this document does absolutely not suggest to use the intermediate step of transferring a layer with a thickness that is substantially greater than that of the ultrathin layer to be obtained.

The present invention aims to overcome the above-mentioned disadvantages and provide a method that can transfer to a support substrate, a transferred layer, and optionally, an interposed layer, which are very thin, i.e., less than about 50 nanometers (50 nm) or even less than 20 nm thick. These layers are termed "ultrathin" layers.

The invention is of particular application to the fabrication of all substrates having a stack of layers some of which are sensitive to degassing.

To this end, the invention concerns a method of producing a structure comprising at least one support substrate and an ultrathin layer deriving from a source substrate, in particular made of a semiconductor material, for applications in the fields of electronics,

optoelectronics or optics, said method comprising the following steps:

a) bonding, by molecular bonding, a support substrate onto one of the faces termed the "front face" of a source substrate having therein a zone of weakness defining with said front face a useful layer termed the "layer to be transferred" the thickness of which is substantially greater than that of said ultrathin layer;

b) detaching said support substrate and said useful layer to be transferred from the remainder of the source substrate, along said zone of weakness, to obtain an intermediate structure comprising at least said transferred useful layer and said support substrate;

c) thinning said transferred useful layer to obtain said ultrathin layer.

Further advantageous and non-limiting characteristics of the invention that can be taken alone or in combination are as follows:

- step a) of molecular bonding the support substrate is carried out on an interposed layer present on the front face of said source substrate;
- the useful layer to be transferred of the intermediate structure is at least three times thicker than said ultrathin layer obtained from the thinning step c);
- said useful layer to be transferred of the intermediate structure is 300 nanometers thick or more and the thickness of the ultrathin layer is 100 nanometers or less;
- the thickness of the ultrathin layer is 50 nanometers or less;
- the thickness of said interposed layer is 50 nanometers or less;

- said interposed layer is a layer of insulating material;
- the interposed layer is a layer of a material selected from silicon oxide, silicon nitride, high permittivity insulating materials, diamond, and combinations of said materials;
- thinning is carried out using at least one of the following techniques: chemical-mechanical polishing, annealing in an atmosphere containing hydrogen, argon or a mixture thereof; sacrificial oxidation; and chemical etching;
- a heat annealing treatment is carried out after bonding step a) and before thinning step c);
- the heat annealing treatment is carried out during detachment step b);
- the heat annealing treatment is carried out before detachment step b);
- the zone of weakness is obtained by atomic species implantation;
- the zone of weakness is a porous layer;
- detachment step b) comprises applying mechanical and/or thermal stresses;
- the transferred useful layer is a layer comprising suspended motifs (suspended layer);
- the source substrate is formed from a material selected from silicon, silicon carbide, germanium, silicon germanium, IV-IV compounds, and III-V compounds, or a combination of said materials;
- the support substrate is formed from a material selected from silicon, silicon carbide, germanium, silicon germanium, IV-IV compounds, and III-V compounds, or a combination of said materials.

Further characteristics and advantages of the invention become apparent from the following description

made with reference to the accompanying drawings, which provide non-limiting illustrations of possible implementations.

In the drawings:

- Figure 1 is a graph showing the total thickness ET of a transferred layer (thin layer and interposed layer) as a function of the number of defects ND observed in the finished structure for two different thicknesses of said interposed layer;
- Figures 2A to 2E and 3A to 3E illustrate successive steps in two variations of the method of the invention.

Figures 2A to 2E and 3A to 3E are diagrams in which the different layers and their thicknesses are not shown to scale and have been deliberately enlarged in places for the purposes of clarification.

Figure 2A, shows a source substrate 1 which has an internal zone of weakness 12 defining two portions, namely a useful layer 13 to be transferred and a remainder 14 or back portion of said source substrate.

It has a face 10 termed the "front face" which is intended to come into contact with a support substrate 3 and is located on the side of the useful layer 13 to be transferred, and an opposed face 11 termed the "back face".

The zone of weakness 12 can be obtained by implanting atomic species.

The expression "implanting atomic species" means any bombardment of atomic species, molecular or ionic, which can introduce said species into a material with a maximum concentration of said species at a predetermined depth with respect to the bombarded surface 10. The molecular or ionic atomic species are introduced into the material with an energy that is also distributed about a maximum.

Atomic species can be implanted in said source substrate 1 using an ion beam implanter or a plasma immersion implanter, for example.

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

Said implantation creates the zone of weakness 12 substantially parallel to the plane of the front face 10, in the bulk of the source substrate 1 at a mean ion penetration depth.

In this regard, reference should be made to the literature concerning the method known under the trade mark "Smart Cut".

The zone of weakness 12 can also be constituted by a porous layer obtained, for example, by the method described in European patent EP-A-0 849 788.

The useful layer 13 to be transferred can also be a layer the front face 10 of which has cavities obtained by etching, said layer being known by the skilled person as a "suspended layer". Such a layer is used in the production of microelectromechanical systems, MEMS.

The support substrate 3 acts as a mechanical support and to this end, its thickness is several hundred micrometers (typically about 300 μm).

It has a front face 30 intended to come into contact with the front face 10 of the source substrate 1 and an opposed face 31 termed the "back face".

The source substrate 1 and the support substrate 3 can be constituted by any material in particular those used routinely in applications in the fields of electronics, optoelectronics or optics, such as semiconductor materials.

By way of illustrative example, it is possible to use silicon, a material that is frequently used in said applications, silicon carbide, germanium, silicon

germanium, IV-IV compounds, and III-V compounds, or a combination of said materials, i.e. a multilayer substrate comprising at least two layers of materials selected from those cited above, as a constituent material of the support substrate 3 and the source substrate 1.

IV-IV compounds are compounds the two elements of which belong to column IVa of the periodic table. III-V compounds are compounds one element of which is from column IIIa of the periodic table and the other of which is from column Va, such as gallium nitride (GaN), gallium arsenide (AsGa), or indium phosphide (InP).

Regardless of the mode of producing the zone of weakness 12, it will be formed in a manner such that the useful layer 13 to be transferred is very thick with respect to the thickness of the final layer which is to be obtained on the support substrate 3.

The characteristics concerning the thickness of said layer to be transferred 13 will be described below.

As shown in Figure 2B, the front face 30 of the support substrate 3 is then bonded by wafer bonding to the front face 10 of the source substrate 1.

Advantageously, an annealing heat treatment is carried out on the stack to strengthen the bonding interface between the front face 10 of the source substrate 1 and the front face 30 of the support substrate 3. Said heat treatment is carried out at a temperature that is suitable as a function of the chemical nature of the materials in contact.

As shown in Figure 2C, the support substrate 3 and the layer to be transferred 13 are then detached from the remainder 14 of the source substrate 1 along the zone of weakness 12.

Detachment is effected, for example, by applying stresses of mechanical origin, which are generally tension and/or bending and/or shear stresses.

Said stresses can be applied, for example, using a drawing rig, or one or more blades introduce into the side of said stack of layers at the zone of weakness 12, or by a jet of fluid (liquid or gas) applied laterally at said same zone of weakness.

The application of said stresses of mechanical origin encourages the propagation of a crack at the zone of weakness 12.

Detachment can also be effected by applying stresses of thermal origin.

The stresses of mechanical origin and of thermal origin can also be combined.

An intermediate structure 4 is thus obtained, comprising the support substrate 3 and the useful layer 13, which is then termed the "transferred layer".

As shown in Figure 2D, a thinning step is then carried out on the transferred useful layer 13 (arrow A) to obtain an ultrathin layer 130 (see Figure 2E).

The final structure obtained, reference number 5, comprises the support 3 and the ultrathin layer 130.

Thinning can be carried out using one of more of the following techniques, for example: chemical-mechanical polishing (CMP), annealing in an atmosphere containing hydrogen and/or argon, sacrificial oxidation, or dry or wet chemical etching.

Chemical-mechanical polishing is a technique combining mechanical polishing carried out by passing a rotary polishing head over the free surface 131 of the transferred layer 13 and chemical polishing implemented by distributing an abrasive in the form of a liquid or paste, such as a colloidal silica, between the surface of said polishing head and the surface 131 to be polished.

Annealing in an atmosphere containing hydrogen and/or argon consists in annealing the intermediate structure 4 in said atmosphere at a temperature of about 1050°C to 1350°C for several tens of seconds to several tens of minutes. Said annealing rearranges the atoms on

the surface 131, which are displaced into a stable energy level, smoothing the surface 131 and thus reducing the thickness (thinning) of the layer 13.

Sacrificial oxidation consists in heating the free surface 131 in an oxidizing atmosphere to form an oxide layer which is removed, and repeating that operation a plurality of times until the desired thickness for the ultrathin layer 130 is reached.

Finally, chemical etching operations comprise wet etching carried out in a bath of chemical products or dry etching carried out in a plasma of a gas, which etches the transferred layer 13. Dry etching can also be carried out by ionic bombardment, for example using argon, which has a mechanical ballistic effect that reduces the thickness of the layer 13 until the ultrathin layer 130 is obtained.

The final thickness of the ultrathin layer 130 obtained from the thinning step is 100 nanometers (100 nm) or less, or even 50 nanometers (50 nm) or less.

The heat annealing treatment described above, carried out to strengthen the bonding interface between the front face 10 of the source substrate 1 and the front face 30 of the support 3 can also be carried out during the detachment step or thereafter, but always before the thinning step. Said annealing heat treatments can also be repeated a plurality of times between bonding and thinning.

It should be noted that when heat annealing is carried out during the detachment step, it is possible to carry out a single heat treatment employing increasing temperatures.

Thus, for example, when the source substrate 1 is silicon, detachment along the zone of weakness 12 is carried out at about 500°C then, when the temperature is at least 1000°C and maintained for several hours, the bonding interface is strengthened.

In accordance with the invention and in contrast to the current state of the art, the method of producing an ultrathin layer 130 consists in passing through an intermediate step (obtaining an intermediate structure 4) during which a useful layer 13, with a thickness that is substantially greater than that of the ultrathin layer 130 to be obtained when the method is completed, is transferred.

The expression "substantially greater" means that the layer to be transferred 13 has a thickness which is sufficient to withstand the different heat treatments of detachment or strengthening of its bonding interface with the support substrate 3 without causing the formation of defects or blisters at said interface.

Preferably, the layer to be transferred 13 is at least three times thicker than the ultrathin layer 130. Preferably again, said layer 13 is 300 nanometers thick or more, while in comparison, the ultrathin layer 130 is 100 nanometers thick or less or even 50 nanometers or less.

Figures 3A to 3E show a variation of the method described with respect to Figures 2A to 2E.

In this variation, an interposed layer 2 is interposed between the front face 10 of the source substrate 1 and the front face 30 of the support surface 3 (see Figure 3B).

As can be seen in Figure 3A, said interposed layer 2 is formed before the step of bonding by wafer bonding, preferably on the front face 10 of the support substrate 1. However, it could also be formed on the front face 30 of the support substrate 3 or on both front faces 10 and 30.

This interposed layer 2 can, for example, be obtained using a chemical vapor deposition technique known as CVD, or by epitaxial techniques, namely metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), or by hydride vapor phase epitaxy (HVPE).

When said interposed layer 2 is an oxide, it can also be obtained by oxidizing the bulk substrate 1.

When the zone of weakness 12 is obtained by implanting atomic species, the interposed layer 2 is preferably deposited prior to implantation. The large rise in temperature connected with the deposition method may be prejudicial to the zone of weakness 12.

In contrast, when the zone of weakness 12 is a porous layer, the interposed layer 2 is deposited after forming said porous zone and the useful layer to be transferred 13, this latter again generally being obtained by epitaxy.

Said interposed layer 2 can, for example, be constituted by a layer of an insulating material, in particular silicon oxide (SiO_2), silicon nitride (Si_3N_4), diamond, an insulating material with a high permittivity, or a combination of said materials, for example silicon oxynitride. Said interposed layer 2 can also be composed of a plurality of different layers of said materials (multilayer).

The other steps of the method are identical to those described above and will not be repeated in detail. It should be noted that after the detachment step shown in Figure 3C, an intermediate structure 4' comprising the support 3, the interposed layer 2 and the transferred layer 13 is obtained.

Following the thinning operation, a support substrate 3 is obtained that supports, in succession, the interposed layer 2 then the ultrathin layer 130 to form a final structure 5'.

Preferably, the interposed layer 2 is thin, i.e., 50 nanometers (50 nm) or less.

The method of the invention can produce a SOI type substrate wherein the silicon oxide interposed layer and the superficial silicon layer are both less than 50 nm thick, which has not been possible until now.

Four particular examples of the method of the invention will now be described.

EXAMPLE 1

Thermal oxidation of a source substrate 1 formed from bulk silicon was carried out to cover it with an interposed layer 2 of silicon oxide (SiO_2) 50 nanometers (50 nm) thick.

The zone of weakness 12 was then formed by implanting hydrogen ions H^+ using an implantation dose of 8×10^{16} H^+/cm^2 and an implantation energy of 210 keV to obtain a layer to be transferred 13 with a thickness of 1.9 micrometers (1.9 μm).

The support substrate formed from bulk silicon was then bonded to said oxide layer 2 by wafer bonding.

The remainder 14 of the source substrate 1 was then detached by a heat treatment at less than 500°C and strengthening the bonding interface using a heat treatment at more than 1000°C.

Finally, thinning was carried out by polishing and sacrificial oxidation to obtain a final structure 5' with an ultrathin silicon layer 130 with a thickness of 50 nm or even 20 nm if said thinning step was continued.

EXAMPLE 2

The procedure of Example 1 was followed, except that the silicon oxide layer 2 was 20 nanometers thick.

EXAMPLE 3:

The procedure of Example 1 was followed, except that the implantation dose was 7×10^{16} H^+/cm^2 and the implantation energy was 160 keV, so that the layer to be transferred 13 was 1.5 micrometers (1.5 μm) thick.

EXAMPLE 4

The procedure of Example 3 was followed, except that the silicon oxide layer 2 was 20 nanometers thick.

CLAIMS

1. A method of producing a structure (5, 5') comprising at least one support substrate (3) and an ultrathin layer (130) deriving from a source substrate (1), in particular made of a semiconductor material, for applications in the fields of electronics, optoelectronics or optics, said method comprising the following steps:

   a) bonding, by molecular bonding, a support substrate (3) onto one of the faces termed the "front face" (10) of a source substrate (1), having therein a zone of weakness (12), defining with said front face (10) a useful layer (13) termed the "layer to be transferred" the thickness of which is substantially greater than that of said ultrathin layer (130);

   b) detaching said support substrate (3) and said useful layer (13) to be transferred from the remainder (14) of the source substrate (1), along said zone of weakness (12), to obtain an intermediate structure (4,4') comprising at least said transferred useful layer (13) and said support substrate (3);

   c) thinning said transferred useful layer (13) to obtain said ultrathin layer (130).

2. A method according to claim 1 for obtaining a structure (5') comprising a support substrate (3), an ultrathin layer (130) deriving from a source substrate (1), in particular formed from a semiconductor material, and an interposed layer (2) inserted between said support substrate (3) and said ultrathin layer (130), characterized in that step a) of molecular bonding the support substrate (3) is carried out on an interposed layer (2) present on the front face (10) of said source substrate (1).

3. A method according to claim 1 or claim 2, characterized in that the useful layer (13) to be transferred of the intermediate structure (4, 4') is at least three times thicker than said ultrathin layer (130) obtained from the thinning step c).

4. A method according to any one of the preceding claims, characterized in that said useful layer (13) to be transferred of the intermediate structure (4, 4') is 300 nanometers thick or more and the thickness of the ultrathin layer (130) is 100 nanometers or less.

5. A method according to claim 3 or claim 4, characterized in that the thickness of said ultrathin layer (130) is 50 nanometers or less.

6. A method according to any one of claims 2 to 5, characterized in that the thickness of said interposed layer (2) is 50 nanometers or less.

7. A method according to any one of claims 2 to 6, characterized in that said interposed layer (2) is a layer of insulating material.

8. A method according to claim 7, characterized in that the interposed layer (2) is a layer of a material selected from silicon oxide, silicon nitride, high permittivity insulating materials, diamond, and combinations of said materials.

9. A method according to any one of the preceding claims, characterized in that thinning is carried out using at least one of the following techniques: chemical-mechanical polishing, annealing in an atmosphere containing hydrogen, argon or a mixture

thereof; sacrificial oxidation; and chemical etching.

10. A method according to any one of the preceding claims, characterized in that a heat annealing treatment is carried out after bonding step a) and before thinning step c).

11. A method according to claim 10, characterized in that the heat annealing treatment is carried out during detachment step b).

12. A method according to claim 10, characterized in that the heat annealing treatment is carried out before detachment step b).

13. A method according to any one of the preceding claims, characterized in that the zone of weakness (12) is obtained by atomic species implantation.

14. A method according to any one of claims 1 to 12, characterized in that the zone of weakness (12) is a porous layer.

15. A method according to any one of the preceding claims, characterized in that detachment step b) comprises applying mechanical and/or thermal stresses.

16. A method according to any one of the preceding claims, characterized in that the transferred useful layer (13) is a layer comprising suspended motifs.

17. A method according to any one of the preceding claims, characterized in that the source substrate (1) is formed from a material selected from silicon, silicon carbide, germanium, silicon germanium, IV-IV

compounds, and III-V compounds, or a combination of said materials.

18. A method according to any one of the preceding claims, characterized in that the support substrate (3) is formed from a material selected from silicon, silicon carbide, germanium, silicon germanium, IV-IV compounds, and III-V compounds, or a combination of said materials.