

THERMAL TREATMENT FOR BONDING INTERFACE STABILIZATION

The invention relates to a method for producing a structure comprising a thin layer of semiconductor material on a substrate, comprising the steps of:

- creating an area of embrittlement in the thickness of a donor substrate;
- bonding of the donor substrate with a support substrate;
- detaching the donor substrate at the level of the area of embrittlement, to transfer part of the donor substrate onto the support substrate and to form the thin layer on the latter;
- thermal treating the structure comprising the thin layer on the support substrate to stabilize the bonding interface between the thin layer and the substrate support.

The invention also relates to the structures obtained by such a process.

Methods of the type mentioned above are already known; for example, they are Smart Cut [™] type methods, the latter correspond to a preferred mode of embodiment of the invention.

Additional details concerning the Smart Cut [™] method will be found in the document, "Silicon-on-Insulator Technology: Materials to VLSI, 2nd Edition," by Jean-Pierre Colinge in "Kluwer Academic Publishers," p. 50 and 51.

Such methods allow structures comprising a thin layer of semiconductor material to be advantageously produced on a

support substrate, particularly SeOI (Semiconductor On Insulator) type structures, in which an insulating layer is inserted between the thin layer and the support substrate.

Structures obtained by such methods are utilized for applications in the microelectronic, optical and/or optoelectronic fields, the thin layer is typically utilized as the active layer for forming components.

Stabilization of the bonding interface between the thin layer and the support substrate proves to be necessary so that the structure obtained after detachment presents mechanical and electrical properties in conformance with the requirements and specifications of the fields of application of the invention.

In particular, this ensures strong adhesion of the thin layer and the support substrate. In the absence of such adhesion, a risk exists that the subsequent steps to form electronic components would lead to delamination of the thin layer at the level of the bonding interface.

In this respect it is noted that in the absence of a treatment to at least reinforce the bonding interface, immersion in an HF bath, directly after detachment, of a structure formed according to a Smart Cut [™] type method, leads to detachment of the thin layer at the periphery of the structure over a radial extent of several microns, or even to the total detachment of the thin layer.

In addition, the quality of the bonding at the level of the bonding interface is likely to modify the behavior of carriers in the thin layer. In order to ensure satisfactory and reproducible electric performance, it is therefore necessary that the bonding interface be stabilized.

It is possible to characterize the correct stabilization of a thin layer/support substrate bonding interface by producing cleavage of the structure and etching the bonding interface by using a Wright type solution (for approximately 10 seconds in the case of an SiO_2/Si interface). If the interface is not stabilized, or is poorly stabilized, the etching reveals a significant number of defects at the level of the interface, or even results in complete etching of the interface. On the contrary, if the interface is perfectly stabilized, no defect is apparent.

More precisely, in the present invention it is considered that an interface is correctly stabilized once, by scanning electronic microscope (SEM) observation of the bonding interface after Wright etching, for example over three fields, each with a width of 3 μm , a number of defects less than or equal to 1 are counted on each field.

An interface presenting no defect/3 fields (of 3 μm in width) will then be considered to be perfectly stabilized.

An interface presenting 1 defect/field (of 3 μm in width) will be considered to be weakly stabilized. However, this weak stabilization will prove to be satisfactory in the fields of application of the invention.

Lastly, an interface presenting more than 1 defect/field (of 3 μm in width) will be considered to be unstabilized.

Figure 1a represents a BOX (Buried Oxide) oxide/silicon Si interface that is perfectly stabilized and does not present any defect. On the other hand, Figure 1b represents a BOX/silicon Si interface that is insufficiently stabilized and presents a defective area Z_d between the BOX oxide layer and the Si substrate, this defective zone Z_d presents

defects revealed by Wright etching (in numbers greater than 1 defect/field observed by SEM).

Partial solutions to the bonding interface stabilization problem have been proposed. They recommend producing "strong" bonding between the donor substrate and the support substrate, typically by heat injection between the bonding and detachment steps or even by performing a preparation treatment of one and/or the other of the surfaces to be bonded before the bonding step.

These solutions allow bonding to be reinforced by increasing the bonding energy between the donor substrate (and, in fine, of the thin layer) and the support substrate. Bonding reinforcement is a microscopic phenomenon and bonding energy may be measured mechanically, for example according to the Maszara blade technique.

A description of this technique will be found in the article, "Silicon-On-Insulator by Wafer Bonding: A Review," by W.P. Maszara in J. Electrochem. Soc., Vol. 138; No. 1, January 1991.

But these solutions do not allow the bonding interface to be stabilized; stabilization is a microscopic phenomenon that reflects the homogeneous establishment of atomic bonds (covalent bonds) between the two substrates assembled over the entire interface. As already mentioned above, the non-establishment of these bonds, even very locally, may be revealed chemically by etching by using the Wright solution.

In other words, a stabilized bonding interface necessarily presents high bonding energy, but the inverse is not true.

In order to produce true stabilization of the bonding interface between the thin layer and the support substrate,

today typically a heat treatment is carried out on the structure obtained after detachment and transfer of the thin layer from the donor substrate to the support substrate.

More precisely, this treatment is furnace annealing of the structure obtained after detachment at a temperature of at least 1000° C for several hours.

This type of long-duration heat treatment will be designated as "stabilization annealing" in the continuation of the description.

By way of example, in the case of SiO₂/Si bonding (the layer of SiO₂ typically formed on the surface of the donor substrate being intended to play the role of the insulating layer between the thin layer and the Si support substrate), stabilization annealing consists of exposing the structure obtained after detachment for two hours at a temperature of 1100° C.

In addition, one may refer to document US 6,403,450 that presents an example of such stabilization annealing.

However, the solution consisting of carrying out such long-duration stabilization annealing to stabilize the bonding interface is not completely satisfactory.

In the first place, the thin layer may not support furnace stabilization annealing for several hours. By way of example, such annealing applied to a Silicon thin layer constraint is likely to generate dislocation type defects in the thickness of the thin layer and to consequently result in relaxation of the constraint.

In addition, stabilization annealing is a long (several hours) operation, consequently presenting a significant

heat budget (temperature/duration pair). Therefore stabilization annealing complicates the manufacturing process of a structure comprising a thin layer on a support substrate and increases the production cost of such a structure.

Furthermore, stabilization annealing is likely, because of the installations necessary for its implementation, to degrade the quality of the thin layer on support substrate structure. In fact, when the temperature exceeds 1000° C, "slip line" type defects may be produced because of the appearance of constraint zones typically located at the level of the extremities of contact points between the structure and the device (known as a "boat") intended to support the structure in the furnace.

Furthermore, it will be revealed that this thin layer quality degradation phenomenon (for example due to the generation of slip lines) is amplified when stabilization annealing is combined with other heat treatments (for example with rapid thermal annealing, as is proposed in document US 2005/0042840). Such a combination, in fact, produces a succession of heat origin constraints that finally combine to degrade the quality of the thin layer.

Therefore a need exists for an alternative technique to post-detachment stabilization annealing carried out in a furnace at a temperature of at least 1000° C for several hours, and more precisely for a technique that allows the bonding interface between a thin layer and a support substrate on which said thin layer was transferred to be stabilized without presenting the abovementioned disadvantages.

The objective of the invention is to respond to this need and the invention proposes for this purpose a method for producing a structure comprising a thin layer of

semiconductor material on a substrate, comprising the steps of:

- creating an area of embrittlement in the thickness of the donor substrate;
- bonding of the donor substrate with a support substrate;
- detaching the donor substrate at the level of the area of embrittlement, to transfer part of the donor substrate onto the support substrate and to form the thin layer on the latter;
- thermal treating the structure obtained after detachment to stabilize the bonding interface between the thin layer and the substrate support;

characterized in that the heat treatment step for stabilizing the bonding interface is carried out by implementing one or more rapid thermal annealing operations.

Some preferred, but not limiting, aspects of this method are the following:

- after detachment, this method furthermore comprises a step of thinning of the thin layer;
- the thinning step is implemented after the first of the rapid thermal annealing operation(s);
- the thinning step comprises a heat treatment operation carried out at a temperature of less than or equal to 1000° C;
- the heat operation of the thinning step is oxidation of the structure obtained after detachment carried out

- at a temperature between 800° C and 1000° C, preferably 950° C;
- following oxidation of the structure obtained after detachment, desoxidation is carried out to remove the layer of oxide formed during the oxidation operation;
 - the heat treatment step for stabilizing the bonding interface is carried out by implementing at least two rapid thermal annealing operations, and the thinning step is carried out between said two rapid thermal annealing operations;
 - a rapid annealing operation is performed by subjecting the structure obtained after detachment to a temperature substantially of between 1200 and 1250° C for a duration substantially of between 5 and 60 seconds;
 - furthermore, the method comprises a bonding energy reinforcement step carried out before detachment, and the heat treatment step for stabilizing the bonding interface is carried out by implementing at least one rapid thermal annealing operation;
 - the bonding energy reinforcement step is implemented before bonding and consists of a plasma treatment of one and/or the other of the surfaces to be bonded;
 - the duration of exposure to plasma is between 5 and 60 seconds, and is preferentially approximately 30 seconds;
 - the plasma is initiated and maintained by application of a radiofrequency power per unit of surface of between 150 and 2800 mW/cm², and preferentially approximately 750 mW/cm²;

- the rapid annealing operation is carried out by subjecting the structure obtained after detachment to a temperature substantially equal to 1200° C for a duration between 5 and 60 seconds, preferentially approximately 30 seconds;

Other aspects, goals and advantages of the present invention will become more apparent upon reading the following detailed description of preferred embodiments of the latter, given by way of non-limiting examples, with reference to the attached drawings in which, outside of Figures 1a and 1b that have previously been discussed, Figure 2a illustrates the bonding interface stabilized by implementing conventional stabilization annealing, while Figures 2a-2c each illustrate the bonding interface stabilized by implementing a possible embodiment of the method according to the invention.

As has already been explained previously, the invention relates to the production of structures comprising a thin layer of semiconductor material on a support substrate, the thin layer being obtained by detachment at the level of a donor substrate in the thickness of which a zone of embrittlement has previously been created.

The zone of embrittlement may be created in the thickness of the donor substrate at a depth near to or greater than the thickness of the thin layer to be transferred by implantation of the atomic species or by formation of a porous layer, or even by any other method that is able to locally fragilize the mechanical bonds in the donor substrate.

Bonding is then achieved by close contact and molecular adhesion of the donor substrate with the support substrate.

Then the donor substrate is detached at the level of the zone of embrittlement, typically by heat and/or mechanical injection, to transfer part of the donor substrate onto the support substrate and to form the thin layer on the latter.

Furthermore, the method according to the invention comprises a heat treatment step for the structure obtained after detachment to stabilize the bonding interface between the thin layer and the support substrate.

More precisely, the invention is directed at a technique allowing the bonding interface to be stabilized, without resorting to stabilization annealing, that is, furnace annealing at a temperature of at least 1000° C for several hours.

For this purpose, the invention proposes performing the heat treatment step for bonding interface stabilization by implementing, after detachment, one or more RTA ("Rapid Thermal Annealing") type operations.

The applicant has noticed that in a particularly surprising manner, it is possible to stabilize the bonding interface by performing the heat stabilization treatment step over a duration that is definitely shorter than that which had been considered to be necessary until now (typically annealing at a temperature over 1000° C for a duration over 30 minutes).

One is reminded here that stabilized interface in the sense of the present invention is understood to refer to an interface presenting microscopic defects following Wright etching with a density that is less than a limit density, typically 1 defect/field (of 3 μm in width) observed by SEM microscope.

In the scope of the present invention, rapid annealing may be carried out in a furnace of those conventionally utilized to carry out RTA. Rapid annealing may also be carried out in an epitaxy frame.

Rapid annealing is performed in controlled atmosphere. This may be an atmosphere comprising a mixture of hydrogen and argon, an atmosphere of pure argon, of pure hydrogen, or even an atmosphere comprising hydrochloric acid.

Generally, the RTA operation is implemented in such a way as to present a heat budget (duration/temperature pair) that is greater than a minimal budget. The RTA temperature must also typically be maintained over 1000° C for approximately several seconds to several minutes.

The stabilization step is preferentially carried out in conjunction with a step, performed after detachment, of thinning of the thin layer.

This thinning step particularly allows the thickness of the thin layer transferred onto the support substrate to be reduced to bring the thin layer to the desired thickness for the final structure.

In addition, it will be noted that beyond the so-called thinning function, the thinning step also allows the surface of the thin layer to be prepared in view of its smoothing, in particular during a subsequent RTA operation.

The thinning step is preferentially, but not exclusively, implemented after the stabilization heat treatment step.

The thinning step is preferentially implemented by performing an oxidation heat treatment of the thin layer (an oxide layer is then formed on the thin layer), then by carrying out a desoxidation operation (to remove the oxide

layer formed during oxidation; for example, by plunging the structure for several minutes in a 10% or 20% hydrofluoric acid solution).

Oxidation is achieved by heating the structure under gaseous oxygen, for example. In any case, thermal oxidation is achieved at a temperature of less than or equal to 1000° C; for example, at a temperature between 800° C and 1000° C, preferably at a temperature of 950° C.

It will be noticed that the act of performing thinning at a temperature of less than or equal to 1000° C allows the generation of slip lines to be limited.

The thinning step is not limited to the oxidation/desoxidation embodiment; it may also be carried out in other ways: for example, by performing dry etching of the thin layer, by implementing annealing in an etching atmosphere (for example, HCl) at temperatures of less than or equal to 1000° C.

According to a first preferred embodiment of the method according to the invention, long-duration stabilization annealing is replaced by performing at least two RTA rapid thermal annealing operations.

More precisely, here two RTA operations are implemented at a higher temperature than the temperature at which stabilization annealing is conventionally carried out.

Taking the example of the stabilization of a conventional SiO₂/Si bonding interface by exposing the structure obtained post-detachment to a temperature of 1100° C for two hours, two RTA operations are carried out in the scope of the invention, each with a duration of 30 seconds, and at a temperature of 1200° C.

However, it will be noted that the invention is not limited to this heat budget (30sec/1200° C) for each of the RTA operations, but also affects the carrying out of RTA operations:

- at temperatures greater than 1200° C, typically up to approximately 1250° C; and/or
- of a duration over 5 seconds, typically up to 60 seconds.

In the scope of a preferential variation of this first embodiment, the thin layer thinning step is carried out between each RTA operation. Thinning is here carried out by the implementation of thermal oxidation at a temperature of less than or equal to 1000° C followed by desoxidation.

According to a second preferred embodiment of the method according to the invention, the stabilization annealing step is replaced by implementation in conjunction with:

- a bonding energy reinforcement step carried out before detachment, and
- a stabilization step for the bonding interface carried out by implementing after detachment at least one rapid thermal annealing operation.

Preferably, the bonding energy reinforcement step is implemented before bonding and consists of plasma treatment of one and/or the other of the surfaces to be bonded.

Therefore, in the scope of this variation, the donor substrate (oxidized or not oxidized in such a way as to form an oxide layer used as the insulating layer inserted between the thin layer and the support substrate) and/or the donor substrate (oxidized or not oxidized for the same

reasons) is (are) exposed to plasma, before close contact with the faces to be bonded.

The duration of exposure to plasma is between 5 and 60 seconds; it typically is approximately 30 seconds.

Equipment conventionally utilized in microelectronics to perform dry etching may be utilized in order to implement this plasma treatment step. In particular, this is equipment allowing RIE (Reactive Ion Etching) type etching to be carried out.

Plasma treatment may be carried out in a vacuum chamber, or even at atmospheric pressure.

A pure gas (typically O_2 , and possibly N_2 , He or Ar), or a gaseous mixture is introduced in the chamber, with a rate of flow on the order of 50 to 500 sccm, in such a way as to establish pressure between 10 and 200 mTorr (typically 50 mTorr).

The plasma may be initiated and then maintained by the application of a radiofrequency power per unit of surface in the range of 150-2800 mW/cm², and typically on the order of 750 mW/cm² (or in the range of 100-2000 W, and typically on the order of 500 W, for a substrate in the form of a 300 mm-diameter wafer).

Plasma treatment allows the bonding interface to be more easily stabilized in temperature. Therefore, in the case where plasma treatment of one and/or the other of the surfaces to be bonded is implemented before bonding according to the conditions indicated previously, the bonding interface stabilization heat treatment step may consist of performing RTA type rapid thermal annealing at 1200° C, for a duration of between 5 and 60 seconds, typically approximately 30 seconds.

In the scope of a preferential variation of this second embodiment, the thin layer thinning step is carried out after the RTA operation. Here thinning is achieved by the implementation of thermal oxidation at a temperature of less than or equal to 1000° C followed by desoxidation.

Returning to the general description of the second embodiment, it is observed that the implementation, before detachment, of a bonding energy reinforcement step has an impact on the ability to easily stabilize the bonding interface through a rapid thermal annealing step performed post-detachment.

It is therefore possible to perform RTA annealing wherein the heat budget is lower than RTA annealing in the scope of the first embodiment. RTA annealing of the second embodiment may therefore be faster (case of the example presented above) or carried out at a lower temperature than the RTA annealing of the first embodiment.

In addition, it is possible in the scope of this second embodiment to highly stabilize the bonding interface by performing a number of rapid thermal annealing operations that is less than the number of operations necessary in the scope of the first embodiment. A single RTA operation is typically only performed in the scope of the second embodiment when two RTA operations would prove to be necessary in the scope of the first embodiment to highly stabilize the bonding interface.

For this reason, Figures 2a-2c illustrate the stabilization of the bonding interface and respectively represent:

- Figure 2a: an Oxide/Silicon interface highly stabilized by the implementation of conventional stabilization annealing for two hours at 1100° C (similar to Figure 1a);

- Figure 2b: an Oxide/Silicon interface weakly stabilized by the implementation, in conformance with the preferential variation of the first embodiment, of two RTA operations at a temperature of 1200° C for 30 seconds, between which is inserted a thinning step carried out by thermal oxidation at a temperature of less than or equal to 1000° C;
- Figure 2c: an Oxide/Silicon interface highly stabilized by the implementation, in conformance with the preferential variation of the first embodiment, of a pre-detachment reinforcement of bonding energy in the form of plasma treatment and of post-detachment RTA sequence (1200° C/30 seconds) and thermal oxidation thinning at a temperature of less than or equal to 1000° C.

It is observed in Figure 2b that stabilization of the bonding interface (such as revealed by Wright etching) is not perfect: a low density of defects may effectively be detected. However, this low presence of defects is not detrimental inasmuch as the stabilization obtained proves to be satisfactory in the fields of application of the invention.

To finish, it is explained that the operations carried out after detachment (such as preferential RTA/thinning/RTA and plasma + RTA/thinning sequence operations), may be completed by additional steps being carried out (for example, additional thinning steps, typically in the form of oxidation/desoxidation) still at a temperature of less than or equal to 1000° C.

The method thus does not comprise any step using a temperature higher than 1000°C, or preferentially 950°C, excepting the one or more rapid thermal annealing operations steps for stabilizing the bonding interface,

i.e. the temperature is kept below 1000°C, or preferentially 950°C, for the set of process steps which correspond to the difference between the whole process and the one or more rapid thermal annealing steps for stabilizing the bonding interface. Hence, thermal oxidations and treatments at temperatures higher than 1000°C, which are additional to RTA steps, are completely suppressed. In particular the temperature is kept below 1000°C, or preferentially 950°C, after detaching the donor substrate at the level of the area of embrittlement.

CLAIMS

1. A method for producing a structure comprising a thin layer of semiconductor material on a substrate, comprising the steps of:
 - creating an area of embrittlement in the thickness of a donor substrate;
 - bonding of the donor substrate with a support substrate;
 - detaching the donor substrate at the level of the area of embrittlement, to transfer a part of the donor substrate onto the support substrate and to form the thin layer on the latter;
 - thermal treating the structure comprising the thin layer on the support substrate to stabilize the bonding interface between the thin layer and the substrate support;

characterized in that the thermal treatment step to stabilize the bonding interface is carried out by implementing one or more rapid thermal annealing operations.
2. The method according to the previous claim, characterized in that the method furthermore comprises a step to thin the thin layer after detachment.
3. The method according to the previous claim, characterized in that the thinning step is implemented after the first of the rapid thermal annealing operation(s).

4. The method according to one of the two previous claims, characterized in that the thinning step comprises a thermal treatment operation carried out at a temperature of less than or equal to 1000° C.
5. The method according to the previous claim, characterized in that the thermal operation for the thinning step is oxidation of the structure obtained after detachment carried out at a temperature between 800° C and 1000° C, preferably 950° C.
6. The method according to the previous claim, characterized in that following oxidation of the structure obtained after detachment, desoxidation is performed to remove the layer of oxide formed during the oxidation operation.
7. The method according to one of claims 2 to 6, characterized in that the thermal treatment step to stabilize the bonding interface is carried out by implementing at least two rapid thermal annealing operations, and in that the thinning step is carried out between said two rapid thermal annealing operations.
8. The method according to the previous claim, characterized in that a rapid annealing operation is carried out by subjecting the structure obtained after detachment to a temperature that is substantially between 1200 and 1250° C for a duration that is substantially between 5 and 60 seconds.
9. The method according to one of claims 2 to 6, characterized in that the method furthermore comprises a step carried out before bonding energy reinforcement detachment, and in that the thermal treatment step for stabilizing the bonding interface is carried out by

implementing at least one rapid thermal annealing operation.

10. The method according to the previous claim, characterized in that the bonding energy reinforcement step is implemented before bonding and consists of a plasma treatment of one and/or the other of the surfaces to be bonded.
11. The method according to the previous claim, characterized in that the duration of exposure to plasma is between 5 and 60 seconds, and is preferentially approximately 30 seconds.
12. The method according to one of the two previous claims, characterized in that the plasma is initiated and maintained by the application of a radiofrequency power per unit of surface between 150 and 2800 mW/cm², and preferentially approximately 750 mW/cm².
13. The method according to any of claims 9 to 12, characterized in that the rapid annealing operation is carried out by subjecting the structure obtained after detachment to a temperature that is substantially equal to 1200° C for a duration of between 5 and 60 seconds, preferentially approximately 30 seconds.
14. The method according to any of claims 1 to 13, wherein the temperature is kept below 1000°C, or preferentially 950°C, after the one or more rapid thermal annealing operations for stabilizing the bonding interface.
15. The method according to claim 14, wherein the temperature is kept below 1000°C, or preferentially 950°C, for process steps corresponding to the difference between the whole process and the one or

more rapid thermal annealing operations for stabilizing the bonding interface.