

PROCESS FOR THE MANUFACTURE OF A HIGH RESISTIVITY SEMICONDUCTOR SUBSTRATE

The present invention relates to a process for the manufacture of a high resistivity semiconductor substrate by layer transfer and relates in particular to the improvement in the substrates of the silicon-on-insulator type having a high resistivity and having a high concentration of interstitial oxygen.

It is generally accepted that the use of high resistivity (or “HR”) semiconductor substrates of the silicon-on-insulator (or “SOI”) type having a high concentration of interstitial oxygen (or “High [O_i]” or else “HiO_i”) requires the use of heat treatments targeted at stabilizing the oxygen present in the silicon (nucleation, precipitation) in order to render the substrate highly resistive.

In this context, “high resistivity” is understood to mean approximately 750 Ω·m or more and “high concentration of interstitial oxygen” is understood to mean approximately 25 ppma or more, i.e. approximately 12.5×10^{17} atoms·cm⁻³ or more.

The abovementioned stabilization stage is conventionally carried out during the stage of sacrificial oxidation of the SOI following a layer transfer carried out, for example, by the known SmartCut® technique. Conventionally, the stabilization stage is more particularly carried out after a smoothing annealing subsequent to the layer transfer, which is generally a rapid annealing, i.e. RTA (“Rapid Thermal Anneal”). The published patent application FR 2 858 462 A1 discloses such a stabilization stage subsequent to a stage of rapid annealing after the layer transfer.

On carrying out the electrical characterization of these materials (pseudo-MOS material), abnormally high interface state densities, typically reaching values of at least 20×10^{11} cm⁻²·eV⁻¹, resulting in a poor mobility of the carriers in the SOI, typically of approximately 400 cm²·V⁻¹·s⁻¹ or less for the electrons, were demonstrated. Additional analyses (C(V) characterization of an MOS capacitor) after removal of the SOI film and aluminium on buried oxide contact have revealed fixed charge values in the buried oxide of at least 5×10^{10} cm⁻² and crest interface state densities of at least 2×10^{11} cm⁻²·eV⁻¹, thus showing that the source of this poor interface quality originated from the interface under the buried oxide.

One hypothesis put forward is that the smoothing annealing (RTA type) results in the modification of the distribution of the unstabilized oxygen in the substrate, thus bringing about an increase in the amount of traps under the buried oxide.

One solution for overcoming this problem lies in the use of HR substrates having a very low concentration of interstitial oxygen (i.e., "Low [Oi]"), namely below approximately 12 ppma, i.e. below approximately 6×10^{17} atoms·cm⁻³, which do not require stabilization annealing of the oxygen in the silicon (nucleation, precipitation). This is because this type of substrate is naturally highly resistive without having to carry out a specific treatment.

However, the disadvantage of the Low [Oi] HR substrates is the very high sensitivity to the propagation of dislocations during heat treatments. For this reason, it is very difficult to obtain defect-free SOIs of sliding plane type using such substrates.

Consequently, an improvement in the quality of the High [Oi] HR substrates remains desirable. It is thus an objective of the present invention to provide a process for the manufacture of a high resistivity semiconductor substrate which makes it possible, in particular for a substrate of the silicon-on-insulator type having a high concentration of interstitial oxygen, to obtain substrates of improved quality with respect to the known state of the art.

The abovementioned objective is achieved by a process for the manufacture of a high resistivity semiconductor substrate comprising the following stages: providing a first substrate with an in-depth weakened layer; providing a second substrate with a layer of an oxide at the surface; attaching the first substrate to the second substrate so as to form a compound substrate comprising a buried oxide layer; and cleaving the compound substrate at the level of the weakened layer. In addition, the process comprises at least one stage of stabilization, in particular a stabilization heat treatment, of the second substrate with the oxide layer before the stage of cleaving at the level of the weakened layer.

The prior art, as represented in particular by FR 2 858 462 A1, teaches the carrying out of a stabilization stage subsequent to a smoothing annealing stage, which is a stage occurring after the cleaving of the compound substrate at the level of the weakened layer. However, the prior art does not teach the carrying out of at least one stabilization stage before the smoothing annealing and in particular before the separation of the weakened layer.

Surprisingly, it has turned out that, by carrying out at least one heat treatment for stabilization of the interstitial oxygen in the silicon (nucleation, precipitation, growth of the precipitates) before the stage of cleaving at the level of the weakened layer, that is to say before carrying out the smoothing annealing of RTA type, it is possible to improve the electrical (in particular interfacial) properties of the resulting substrate, especially in the case of a high concentration of interstitial oxygen. Preferably, the said at least one stabilization stage can thus be a stage of nucleation, precipitation and growth of the precipitates, in particular a heat treatment comprising several stationary temperature phases.

In other words, the present invention proposes to carry out the treatments targeted at rendering a substrate having a high concentration of interstitial oxygen highly resistive (nucleation, precipitation), before any smoothing treatment of RTA type, in particular before the cleaving stage, during the preparation of a substrate of SOI type. The present invention thus makes it possible to obtain electrical characteristics compatible with the preparation of transistors of CMOS type on such substrates.

Consequently, the solution provided by the present invention advantageously makes it possible to use substrates having a high concentration of interstitial oxygen in the preparation of an SOI substrate for applications of RF, photonic, imaging, digital, and the like, type, without having recourse to substrates having a very low concentration of interstitial oxygen which are very sensitive to heat treatments in terms of deformations and defects induced.

According to possible alternative forms of embodiments of the present invention, and without implied limitation:

In some embodiments, the weakened layer can be provided by ion implantation in the first substrate. It is thus possible to carry out the layer transfer by a technique of the SmartCut® type.

In some embodiments, the said at least one stage of stabilization of the second substrate with the oxide layer can be carried out preferably before the stage of attachment of the two substrates. Thus, the said at least one stabilization stage can, in all cases, be carried out before the cleaving and thus before any smoothing annealing subsequent to the cleaving.

In some embodiments, the first substrate, in other words the donor substrate in a layer transfer, can comprise a semiconductor material, in particular silicon, germanium or a compound of silicon and of germanium. More generally, the donor substrate can comprise one or more alloys of semiconductors III-V and/or one or more alloys of semiconductors of Group IV.

In some embodiments, the second substrate can comprise silicon, in particular having a high concentration of interstitial oxygen. Preferably, the second substrate can comprise silicon with a concentration of interstitial oxygen of at least approximately $12 \times 10^{17} \text{ atoms}\cdot\text{cm}^{-3}$.

In some embodiments, the said at least one stabilization stage is a heat treatment comprising several stationary phases at temperatures within the range from approximately 650°C to approximately 1200°C.

In some embodiments, the duration of a stationary temperature phase is within the range extending from approximately 30 min to approximately 10 h, preferably within the range extending from approximately 1 h to approximately 8 h.

In some embodiments, the atmosphere of a stationary temperature phase can be of oxidizing type, in particular based on water and on oxygen, or of nonoxidizing type, in particular neutral type, with a gas based on argon.

The above parameters for the stationary temperature phases gave the results which make it possible to improve the electrical (in particular interfacial) properties of the resulting substrate, especially in the case of a high concentration of interstitial oxygen.

In some embodiments, the process can additionally comprise at least one stage of smoothing annealing, in particular a rapid thermal annealing, after the stage of cleaving the compound substrate at the level of the weakened layer. It is thus possible to improve the surface roughness of the substrate after the layer transfer.

In some embodiments, the said at least one stage of smoothing annealing can be carried out at a temperature within the range from approximately 1075°C to approximately 1250°C, preferably from approximately 1175°C to approximately 1230°C, in particular a temperature of approximately 1200°C.

In some embodiments, the said at least one stage of smoothing annealing can be carried out for a period of time within the range of approximately 15 s to approximately

120 s, preferably from approximately 20 s to approximately 90 s, in particular a period of time of approximately 30 s.

In some embodiments, the said at least one stage of smoothing annealing can be carried out under an atmosphere of the nonoxidizing type, in particular comprising argon and/or hydrogen in a composition which can range from 0% to approximately 50% of hydrogen.

In some embodiments, the process can additionally comprise a stage of recycling a residue of the first substrate after the stage of cleaving the compound substrate at the level of the weakened layer. It is thus possible to reuse the residue again as donor substrate for other layer transfer processes.

The invention will be explained in more detail in the continuation by means of advantageous embodiments and with the support of the following accompanying figures, in which:

- Fig. 1 diagrammatically illustrates stages of a process for the manufacture of a high resistivity semiconductor substrate according to a first exemplary embodiment of the present invention; and
- Fig. 2 diagrammatically illustrates stages of a process for the manufacture of a high resistivity semiconductor substrate according to a second exemplary embodiment of the present invention.

In the following description of exemplary embodiments of a process for the manufacture of a high resistivity semiconductor substrate according to the present invention, analogous reference signs can be used to denote the same elements repeated in the different embodiments. Furthermore, the description of elements already described may be omitted for the sake of conciseness.

A first exemplary embodiment of a process for the manufacture of a high resistivity semiconductor substrate will now be described with reference to Fig. 1. In this embodiment, the transfer of a layer of a semiconductor material will be carried out from a donor substrate towards a receiver substrate.

As illustrated in Stage (I) of Fig. 1, a donor substrate 101 comprising an in-depth weakened layer 102 is provided for the purpose of carrying out a layer transfer towards a receiver substrate. The substrate 101 can be a semiconductor material, for example

silicon, germanium or a compound of silicon and of germanium. More generally, the donor substrate can comprise one or more alloys of semiconductors III-V and/or one or more alloys of semiconductors of Group IV.

As illustrated in Stage (II) of Fig. 1, a substrate 103 comprising an oxide layer 104 at the surface is also provided for the purpose of receiving a transferred semiconductor layer. The substrate 103 can comprise silicon and in particular interstitial oxygen with a concentration of at least approximately 12×10^{17} atoms·cm⁻³. The oxide layer 104 can be a layer of a natural oxide or a layer of SiO₂ obtained by growth or else deposited. The layer 104 can also be, for example, an insulator used in a semiconductor of alumina (Al₂O₃) type or also of nitride type, such as Si₃N₄.

As illustrated in Stage (III) of Fig. 1, before the transfer of a layer from the donor substrate 101 and in particular before being attached to the latter, the substrate 103 comprising the oxide layer 104 at the surface is subjected to at least one stage of stabilization treatment of the interstitial oxygen. This stage can thus be a stage of nucleation, precipitation and growth of the precipitates. It can thus be a heat treatment comprising several stationary temperature phases. This treatment, in particular a stationary temperature phase, can be carried out under an atmosphere of oxidizing type, in particular based on water and on oxygen, or else under an atmosphere of nonoxidizing type, in particular of neutral type, with a gas based on argon. The substrate 103 comprising the oxide layer 104 can thus be subjected to a temperature, in particular to stationary temperature phases, within the range from approximately 650°C to approximately 1200°C. Furthermore, this treatment, in particular each stationary temperature phase, can last for approximately 30 min to approximately 10 h, preferably from approximately 1 h to approximately 8 h.

Subsequently, after the stabilization treatment, as illustrated in Stage (IV) of Fig. 1, the donor substrate 101 is attached, in particular adhesively bonded, for example by molecular adhesion or any other method of adhesively bonding semiconductors, to the receiver substrate 103 via the oxide layer 104, so as to form a compound substrate 105 of the SOI type with a buried oxide layer 104.

Subsequently, after the adhesive bonding stage, as illustrated in Stage (V) of Fig. 1, a portion 1012 of the donor substrate 101 is detached from the compound substrate 105 by cleaving at the level of the in-depth weakened layer 102 so as to leave a transferred layer 1011 of the donor substrate 101 attached to the receiver substrate 103

via the oxide layer 104, thus forming a new compound substrate 106 comprising the transferred layer 1011. It is then possible to improve the surface roughness of the transferred layer 1011 by subjecting the compound substrate 106 to one or more smoothing heat treatments, in particular of the rapid annealing, i.e. RTA, type. Furthermore, the residue 1012 of the donor substrate 101 can be recycled to form a new donor substrate in another layer transfer process.

In all cases, the compound substrates 105 and 106 are both substrates of HiOi HR SOI type, namely of the type of high resistivity silicon-on-insulator having a high concentration of interstitial oxygen. Given that the said at least one stage of stabilization of the interstitial oxygen has been carried out before the layer transfer, in other words before the cleaving stage, and thus before any smoothing annealing, it is possible to obtain HiOi HR SOI substrates with interface state densities of less than $5 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ and mobilities of the carriers in the SOI of greater than $700 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for the electrons. After removal of the SOI film and aluminium on buried oxide contact, the fixed charge values in the buried oxide can then be less than $3 \times 10^{10} \text{ cm}^{-2}$ and the crest interface state densities can be less than $5 \times 10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$.

In other words, the electrical (in particular interfacial) properties of the compound substrates 105 and 106 are very markedly improved in comparison with HiOi HR SOI substrates obtained by conventional methods, that is to say for which the stabilization stage would have been carried out after the smoothing annealing(s).

A second exemplary embodiment of a process for the manufacture of a high resistivity semiconductor substrate will now be described with reference to Fig. 2. The second embodiment repeats all the characteristics of the first embodiment and in addition gives details of optional process stages.

As illustrated in Stage (I) of Fig. 2, a donor substrate 201, which can be the same as the donor substrate 101 of the first embodiment, is first of all provided. The substrate 201 can thus also be a semiconductor material, such as silicon, germanium or a compound of silicon and of germanium. More generally, the donor substrate can comprise one or more alloys of semiconductors III-V and/or one or more alloys of semiconductors of Group IV.

Stage (II) of Fig. 2 illustrates that the donor substrate 201 can subsequently be subjected to a stage of in-depth weakening in order to provide an in-depth weakened layer 202 for the purpose of carrying out a layer transfer towards a receiver substrate, as in the

first embodiment. This stage can be carried out in particular by ion implantation, especially by implantation of ionic entities, such as H^+ and/or He^+ .

As illustrated in Stage (III) of Fig. 2, a substrate 203 comprising a layer of oxide 204 at the surface is also provided for the purpose of receiving a transferred semiconductor layer. Just like the substrate 103 of the first embodiment, the substrate 203 of the second embodiment can thus comprise silicon and in particular interstitial oxygen with a concentration of at least approximately $12 \times 10^{17} \text{ atoms}\cdot\text{cm}^{-3}$. Still analogously to the first embodiment, the layer of oxide 204 can once more be a layer of a natural oxide, a layer of SiO_2 , obtained by growth or else deposited, or also an insulator used in semiconductors of alumina (Al_2O_3) type or of nitride type, such as Si_3N_4 .

As illustrated in Stage (IV) of Fig. 2, before the transfer of a layer from the donor substrate 201 and in particular before being attached to the latter, the substrate 203 comprising the layer of oxide 204 at the surface is subjected to at least one stage of stabilization treatment of the interstitial oxygen. Analogously to the first embodiment, in the second embodiment the stabilization treatment can be a stage of nucleation, precipitation and growth of the precipitates. It can thus be a heat treatment comprising several stationary temperature phases. This treatment, in particular a stationary temperature phase, can be carried out under an atmosphere of oxidizing type, in particular based on water and on oxygen, or else under an atmosphere of nonoxidizing type, in particular of neutral type, with a gas based on argon. The substrate 203 comprising the layer of oxide 204 can thus also be subjected to a temperature, in particular to stationary temperature phases, within the range from approximately 650°C to approximately 1200°C . Furthermore, this treatment, in particular each stationary temperature phase, can last from approximately 30 min to approximately 10 h, preferably from approximately 1 h to approximately 8 h.

After the stabilization treatment, as illustrated in Stage (V) of Fig. 2, analogously to the adhesive bonding stage of the first embodiment, the donor substrate 201 and the receiver substrate 203 are adhesively bonded at the level of the layer of oxide 204, so as to form a compound substrate 205 of the SOI type with the layer of buried oxide 204. In this instance also, the adhesive bonding can be carried out by molecular adhesion or any other method for the adhesive bonding of semiconductor layers.

Subsequently, as illustrated in Stage (VI) of Fig. 2, the stage of adhesive bonding is also followed by a stage of cleaving in which a portion 2012 of the donor substrate 201

is detached from the compound substrate 205 by cleaving at the level of the in-depth weakened layer 202, so as to leave a transferred layer 2011 of the donor substrate 201 attached to the receiver substrate 203 by the oxide layer 204, thus forming a new compound substrate 206 comprising the transferred layer 2011. Such a cleaving stage can be carried out by subjecting the compound substrate 205 to a temperature in a range from approximately 300°C to approximately 600°C for a period of time of approximately 30 min to approximately 5 h, under a neutral atmosphere of N₂ or of Ar.

Subsequently, after the cleaving stage, Stage (VII) of Fig. 2 illustrates an optional subsequent smoothing stage which makes it possible to improve the roughness of the exposed surface 207 of the transferred layer 2011. This stage can be carried out by carrying out a heat treatment comprising one or more annealings, preferably one or more rapid annealings, i.e. RTAs. The compound substrate 206 can then be exposed to a temperature within a range from approximately 1075°C to approximately 1250°C, preferably from approximately 1175°C to approximately 1230°C, in particular a temperature of approximately 1200°C, this being done for a period of time within the range from approximately 15 s to approximately 120 s, preferably from approximately 20 s to approximately 90 s, in particular a period of time of approximately 30 s, under an atmosphere of the nonoxidizing type, in particular comprising argon and/or hydrogen in a composition which can range from 0% to approximately 50% of hydrogen.

Finally, as mentioned above, the residue 2012 of the donor substrate 201 can also be recycled in order to form a new donor substrate in another layer transfer process.

Thus, analogously to the first embodiment, it is possible in the second embodiment to obtain compound substrates 205 and 206 of HiOi HR SOI type, namely of the type of high resistivity silicon-on-insulator having a high concentration of interstitial oxygen. In particular, given that the said at least one stage of stabilization of the interstitial oxygen was carried out before the layer transfer, in other words before the cleaving stage, and thus before any smoothing annealing, just as in the first embodiment, it is possible in the second embodiment to obtain HiOi HR SOI substrates with interface state densities of less than $5 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ and mobilities of the carriers in the SOI of greater than $700 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for the electrons. After removal of the SOI film and aluminium on buried oxide contact, the fixed charge values in the buried oxide can then be less than $3 \times 10^{10} \text{ cm}^{-2}$ and the crest interface state densities can be less than $5 \times 10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$.

In other words, just like those of the compound substrates 105 and 106, the electrical properties (in particular interfacial properties) of the compound substrates 205 and 206 are also very markedly improved in comparison with HiOi HR SOI substrates obtained by conventional methods, that is to say for which the stabilization stage would have been carried out after the smoothing annealing(s).

Furthermore, the different examples of embodiments of the present invention can be combined with one another in order to create other embodiments still according to the present invention.

CLAIMS

1. A method of forming a semiconductor structure, the method comprising:

providing a first substrate with an in-depth weakened layer;

providing a second substrate with an oxide layer at a surface thereof;

attaching the first substrate to the second substrate to form a compound substrate comprising a buried oxide layer, the first substrate comprising the in-depth weakened layer, the second substrate comprising the oxide layer;

stabilizing at least the second substrate with the oxide layer at the surface; and

after stabilizing at least the second substrate, cleaving the compound substrate at the weakened layer to form a semiconductor structure.
2. The method of claim 1, wherein stabilizing at least the second substrate comprises stabilizing at least the second substrate before attaching the first substrate to the second substrate.
3. The method of claim 1, wherein stabilizing at least the second substrate comprises nucleation, precipitation of precipitates, and growth of the precipitates.
4. The method of claim 1, wherein stabilizing at least the second substrate comprises heat treating at least the second substrate at each of a plurality of temperatures within a range from approximately 650°C to approximately 1,200°C.
5. The method of claim 4, wherein each of the plurality of temperatures is maintained for a duration with a range extending from approximately 30 minutes to approximately 10 hours.
6. The method of claim 4, wherein heat treating at least the second substrate comprises exposing at least the second substrate to a nonoxidizing atmosphere.
7. The method of claim 4, wherein heat treating at least the second substrate comprises exposing at least the second substrate to an oxidizing atmosphere.

8. The method of claim 7, wherein exposing at least the second substrate to an oxidizing atmosphere comprises exposing at least the second substrate to an atmosphere comprising water and oxygen.

9. The method of claim 1, further comprising forming the weakened layer by ion implantation in the first substrate.

10. The method of claim 1, further comprising annealing the semiconductor substrate after cleaving the compound substrate at the weakened layer.

11. The method of claim 10, wherein annealing the semiconductor structure comprises exposing the semiconductor structure to a temperature within a range from approximately 1,075°C to approximately 1,250°C.

12. The method of claim 11, wherein annealing the semiconductor structure comprises exposing the semiconductor structure to a temperature within a range from approximately 1,175°C to approximately 1,230°C.

13. The method of claim 10, wherein annealing the semiconductor structure comprises exposing the semiconductor structure to an annealing condition for a period of time within a range from approximately 15 seconds to approximately 120 seconds.

14. The method of claim 13, wherein annealing the semiconductor structure comprises exposing the semiconductor structure to an annealing condition for a period of time within a range from approximately 20 seconds to approximately 90 seconds.

15. The method of claim 10, wherein annealing the semiconductor structure comprises exposing the semiconductor structure to a nonoxidizing atmosphere.

16. The method of claim 15, wherein exposing the semiconductor structure to a nonoxidizing atmosphere comprises exposing the semiconductor structure to an atmosphere comprising at least one gas selected from the group consisting of hydrogen and argon.

17. The method of claim 16, wherein exposing the semiconductor structure to a nonoxidizing atmosphere comprises exposing the semiconductor structure to an atmosphere comprising approximately 50% hydrogen or less.

18. The method of claim 1, further comprising attaching a residue of the first substrate to a third substrate after cleaving the compound substrate at the weakened layer, the third substrate comprising a layer of an oxide.

19. The method of claim 1, wherein the first substrate comprises a semiconductor material.

20. The method of claim 1, wherein the second substrate comprises silicon.