# A METHOD OF PRODUCING A LAYER OF CAVITIES

## Technical field and prior art

The present invention relates to a method of producing cavities disposed in an insulating layer of oxide or nitride.

During the fabrication of multilayer structures such as SeOI (semiconductor on insulator) type structures for electronic, microelectronic, and optoelectronic applications, it is routine to interpose insulating layers between wafers of semiconductor materials such as silicon wafers, for example.

Further, it may be necessary to form microcavities or microbubbles in the insulating structure. This applies in particular when the structure is to be capable of being taken apart at the insulating layer, as described in the document WO-A-2005/034218.

The document "Structural and nuclear characterizations of defects created by noble gas implantation in silicon oxide" by H. Assaf et al, Nuclear Instruments and Methods, B 253 (2006), 222-26, for example, describes a method of forming microbubbles in a layer of silicon oxide ($SiO_2$) in order to reduce the value of the dielectric constant $\underline{k}$ of the oxide layer and, as a result, its permittivity. The method described in that document consists in implanting a layer of $SiO_2$ formed on a silicon substrate with heavy rare gas ions such as xenon. Said implantation allows microbubbles to be formed in the $SiO_2$ layer.

However, that method requires the use of heavy rare gas ions, which involves the use of particular ion sources and of more expensive equipment (implanter). Implantation with heavy ions requires higher implantation energy and generates more damage in the implanted material compared with implantation carried out with hydrogen or helium ions, for example. Further, with such ions, it is difficult to control the implantation depth

of the ions in the oxide layer and, as a result, the zone over which the microbubbles extend.

There now exists a need to be able to form insulating layers comprising cavities in substrates in a manner that is accurate and economical.

**Summary of the invention**

The aim of the present invention is to propose a solution that enables cavities to be produced in an insulating layer without the above-mentioned disadvantages.

To this end, the invention proposes a method of producing a layer of cavities in a structure comprising at least one substrate formed from a material that can be oxidized or nitrided, the method comprising the following steps:

- implanting ions into said substrate in order to form an implanted ion concentration zone at a predetermined mean depth;
- heat treating the implanted substrate to form a layer of cavities at the implanted ion concentration zone; and
- forming an insulating layer in said substrate by thermochemical treatment from one surface of said substrate, said insulating layer that is formed extending at least partially into the layer of cavities.

Thus, by producing a layer of cavities before forming the insulating layer, it is possible to accurately control the formation of the layer of cavities since implantation is carried out into a homogeneous substrate without having to use special ions such as heavy rare gas ions for implantation. Further, the (total or partial) degree by which the layer of cavities overlaps the insulating layer may also be accurately controlled since all that is required is to stop the insulating layer formation front at the desired region in the substrate.

In one aspect of the invention, the insulating layer formed by thermochemical treatment extends over the entire layer of cavities.

In one implementation of the invention, the thermochemical treatment of the surface substrate is carried out in an oxidizing atmosphere in order to form an insulating layer of oxide.

In another implementation of the invention, the thermochemical treatment of the substrate surface is carried out in a nitriding atmosphere in order to form an insulating layer of nitride.

In a particular aspect of the invention, one or more dopants are introduced into the substrate during thermochemical treatment. This or these dopants may in particular introduce positive or negative charges into the cavities of the insulating layer.

The invention also proposes a method of producing a multilayer structure, comprising at least bonding a first structure onto a second structure, the second structure comprising a substrate including a layer of cavities and an insulating layer formed in accordance with the method of the invention for forming a layer of cavities.

The first structure may in particular comprise a layer of semiconductor material such as a layer of silicon. Thus, a multilayer SeOI type structure is formed with a buried insulating layer including cavities.

The invention also provides a composite structure comprising a substrate constituted by a material that is capable of being oxidized or nitrided, the structure further comprising an insulating layer formed by thermochemical treatment of the material of said substrate, the insulating layer including a layer of cavities, the structure being characterized in that the cavities of said layer are oblong in shape and in that said cavities are oriented in the same direction.

The insulating layer may be a layer of oxide or nitride.

In one aspect of the invention, the cavities of the layer of cavities contain one or more dopants selected from at least: nitrogen, boron, arsenic, phosphorus, antimony, aluminum, gallium, iron, nickel, and cobalt.

**Brief description of the figures**

The characteristics and advantages of the present invention become apparent from the following description made by way of non-limiting indication with reference to the accompanying drawings in which:

- Figures 1A to 1C are diagrammatic sectional views showing the formation, in a silicon substrate, of a layer of cavities and of an insulating layer in accordance with one implementation of the invention;
- Figure 2 is a flow chart of the steps carried out in Figures 1A to 1C;
- Figures 3 to 5 are microphotographs taken with a transmission electron microscope and showing a layer of microcavities formed in a silicon substrate, which substrate is then being oxidized in accordance with one implementation of the method of the invention;
- Figure 6 is a graph showing the size and the distribution of microcavities formed in an oxidized silicon substrate in accordance with one implementation of the method of the invention;
- Figure 7 is a diagrammatic view of a composite structure in accordance with one implementation of the invention.

**Detailed description of implementations of the invention**

The present invention is of general application to any material that can be implanted with ionic species and that is capable of being oxidized and/or nitrided. By way of non-limiting example, the following materials may be used to carry out the method of the invention:

- oxidizable and/or nitridable metals and metal alloys (iron, zinc, copper, steel, titanium, zirconium, etc);
- crystalline semiconductor materials such as silicon, III/V materials (GaAs, GaN, etc), germanium and its compounds such as SiGe;
- silicon carbide (SiC).

One implementation of the method of the invention is described below with reference to Figures 1A to 1C and 2, applied to formating a layer of cavities in an oxide layer of a silicon substrate.

In particular, the method of the invention comprises the steps of ion implantation, heat treatment to develop the cavities, and thermochemical treatment to form a layer of oxide or nitride. The ion implantation of a substrate, for example using hydrogen ($H^+$) and/or helium (He) ions, is carried out with an implantation dose in the range $1 \times 10^{15}$ to $1 \times 10^{19}$ atoms/$cm^2$ [atoms/square centimeter] and with an implantation energy in the range 10 keV [kiloelectron volts] to 200 keV. The heat treatment to develop the cavities in the implanted substrate is generally carried out in the range 700°C to 1300°C, preferably in the range 900°C to 1200°C, for a period in the range 10 minutes to 20 hours, preferably in the range 1 hour to 10 hours. The oxidation/nitriding thermochemical treatment is generally carried out in the range 700°C to 1300°C for oxidation and in the range 900°C to 1300°C for nitriding, the treatment period generally being several hours.

As illustrated in Figure 1A, the method commences by implanting a silicon substrate 101 in the form of a wafer having, for example, a thickness of 0.7 mm [millimeter] and a diameter in the range 50 mm to 300 mm (step S1). During implantation, the silicon substrate 101 undergoes bombardment with ions 10, for example He ions. The ions 10 penetrate into the substrate 101 and are brought to a halt at a predetermined depth therein, creating an

implanted ion concentration zone 102 at a predetermined mean depth in the substrate. The term "mean depth" is used for the concentration zone because the implanted ions lose their energy via a succession of impacts with the atoms of the crystal lattice of the silicon and they do not all stop at exactly the same depth. In other words, the implanted ion concentration zone extends over a certain thickness in the substrate.

As is well known, the mean depth of the implanted ion concentration zone in the substrate is determined by the implantation energy, naturally taking into account the nature of the ions used and the implanted material. The degree of concentration of the ions in this zone is determined by the implantation dose employed. In the example described here, implantation is carried out with He ions and with an implantation energy of 75 keV and an implantation dose of approximately $8\times10^{16}$ atoms/$cm^2$. With these implantation conditions, an implanted ion concentration zone 102 is formed at a mean depth from the surface of the substrate of a few hundred nanometers, the zone extending over a thickness of approximately one hundred nanometers.

Once the silicon substrate 101 has been implanted, heat treatment or annealing is carried out in order to use the defects created by the ions in the implanted ion concentration zone 102 to form a layer 103 comprising microcavities or microbubbles 104 (Figure 1B, step S2). In the example described here, the heat treatment is carried out at a temperature of 950°C for a period of approximately 8 hours. The layer 103 has a thickness in the range 190 nm [nanometer] to 220 nm. For substrates formed from different materials and/or for different implantation species, the temperature and period for the heat treatment to develop microcavities should be adjusted.

The method is then continued by forming a layer 105 of silicon oxide ($SiO_2$)(Figure 1C, step S3). More

precisely, the substrate 101 is oxidized from one of its surfaces, here the implanted surface of the substrate. To this end, the substrate undergoes a thermochemical treatment that consists in placing the substrate in a chamber maintained at a predetermined temperature and in which the surface of the substrate is exposed to an oxidizing atmosphere. By way of non-limiting examples, the oxidizing atmosphere may be constituted from gaseous oxygen ($O_2$), optionally with hydrogen, and/or hydrogen chloride (HCl), and/or argon (Ar). The oxidizing atmosphere may also be composed of water vapor ($H_2O$), optionally with hydrogen, and/or hydrogen chloride (HCl), and/or argon (Ar).

The duration of the thermochemical treatment depends on the thickness of the $SiO_2$ layer 105 that is to be obtained as well as on the rate of advance of the oxidation front into the silicon substrate 101. The duration of the thermochemical oxidation treatment may be adjusted in order to stop the oxidation front within the layer 103. Under such circumstances, microcavities exist both in the oxide layer formed and in a subjacent portion of the silicon substrate. However, the duration may be prolonged in order to stop the oxidation front beyond the layer 103 such that all microcavities are included in the oxide layer.

In the example described here, the formed oxide layer at least partially overlaps the layer 103 in order to have at least a fraction of the microcavities 104 included in the $SiO_2$ layer 105. To this end, the silicon substrate 101 is treated in an atmosphere principally containing gaseous oxygen at a temperature of 950°C for a period of 3 hours. These treatment conditions mean that an $SiO_2$ layer 105 with a thickness $e$ of 690 nm [nanometer] is formed. The techniques and conditions for carrying out said thermochemical oxidation treatment are well known to the skilled person and are not described in further detail, for the purposes of simplification.

As can be seen in Figure 1C, a structure 100 is obtained comprising an $SiO_2$ layer 105 on a layer of silicon 106 corresponding to the portion of silicon substrate 101 that has not been oxidized, the structure further comprising a buried microcavity layer 103 that is present in both the $SiO_2$ layer 105 and in the silicon layer 106.

Hence, in accordance with the invention, cavities are transferred from a material that is capable of being oxidized or nitrided to an oxide layer or a nitride layer respectively. In particular, surprisingly, the cavities are conserved during the thermochemical oxidation or nitriding treatment. Oxidizing the portion of silicon substrate 101 including the microcavities 104 does not cause them to disappear, which means that an insulating layer can be formed, here an oxide layer, which layer includes microcavities that have already been formed in the silicon substrate. However, the microcavities 104a present in the $SiO_2$ layer 105 may change in volume and shape compared with the microcavities 104b still present in the non-oxidized silicon substrate portion. During oxidation, the microcavities affected by the oxidation front tend to be oxidized or nitrided to a greater or lesser extent as a function of the crystalline axes, but with the cavities, still being present after the treatment.

Measurements of the shape, size, and density of the microcavities have been carried out on a silicon substrate which had undergone implantation, a heat treatment to develop microcavities, and an oxidation under the same operating conditions as those described above.

The mean thickness of the layer of microcavities was approximately 200 nm.

As can be seen in Figures 3 to 5, the microcavities present in the oxide layer are oblong or ellipsoidal in shape, i.e. they have an elongate shape principally

characterized by a length and a width. These cavities have a width mainly in the range 1 nm to 30 nm and a length mainly in the range 10 nm to 60 nm. The mean density of the microcavities in the oxide layer is $1.2\times10^{15}$ cavities.$cm^{-3}$.

The microcavities present in the silicon layer (non-oxidized substrate portion) have a truncated polyhedral shape and a diameter that is principally in the range 25 nm to 35 nm (Figures 3 to 5). The mean density of the microcavities in the silicon layer is $3.7\times10^{15}$ cavities.$cm^{-3}$.

The overall mean density of the microcavities in the two layers (oxide and silicon layers) is $2.5\times10^{15}$ cavities.$cm^{-3}$.

Figure 6 illustrates the size distribution of the microcavities in the oxide layer and in the silicon layer. As can be seen in Figure 6, the diameter of the cavities present in the silicon layer is distributed in accordance with a Gaussian distribution.

Ion implantation may be carried out with different species. In particular, it may be carried out with hydrogen and/or helium ions. Implantation of helium has the particular advantage of it being possible to implant a large dose of ions without the risk of fracturing the substrate.

In another implantation of the invention, the oxide layer including all or some of the microcavities may be replaced by a layer of nitride.

Under such circumstances, in order to form a layer of nitride with microcavities, the above-described steps of implantation and heat treatment to develop microcavities are carried out on a substrate that is capable of being implanted and nitrided. In order to form a layer of nitride instead of a layer of oxide, during the thermochemical treatment, the oxidizing atmosphere used in the above-described thermochemical treatment needs to be replaced by a nitriding atmosphere.

Particular non-limiting examples of a nitriding atmosphere are those comprising nitrogen, ammonia ($NH_3$), silane ($SiH_4$), etc. In similar manner to the thermochemical oxidation treatment, the nitriding front is stopped at a desired depth in the substrate, i.e. within the layer of microcavities if microcavities are desired both in the nitrided layer and in the non-nitrided portion of substrate, or beyond the layer of microcavities if all of the microcavities are to be included in the nitrided layer.

With an initial substrate of silicon, for example, after implantation and heat treatment to develop the microcavities of the substrate, it is possible to form a layer of silicon nitride ($Si_3N_4$) includes all or some of the microcavities by exposing the substrate to a nitrogen atmosphere maintained at a temperature in the range 900°C to 1300°C.

The structure obtained in accordance with the method of the invention, i.e. a substrate comprising a layer of microcavities and a layer of oxide or nitride extending at least partially into the layer of microcavities, may be used for a variety of applications.

In particular, with an initial substrate formed from a semiconductor material (silicon, germanium, etc), said structure may be bonded onto a second substrate in order to form a SeOI (semiconductor on insulator) type structure. The buried insulating layer then includes cavities.

By bonding the structure of the invention onto another substrate, it is possible to form a releasable structure. The layer of oxide or nitride including the microcavities forms a weakened interface that may be ruptured under the action, for example, of a mechanical detaching force, for example by introducing a blade into the microcavities and using it to exert a force to separate the substrates. The risks of unwanted fracture during the heat treatments are very low since

microcavities do not develop, or develop only to a slight extent, in an oxide or a nitride. In this application, the microcavities are preferably entirely contained in the layer of oxide or of nitride.

Hence, a releasable substrate is provided that is highly tolerant to high temperatures and, as a result, to the fabrication of electronic components, for example of the complementary metal oxide semiconductor (CMOS) type requiring temperatures of the order of 900°C. The substrate may then be fractured mechanically or chemically, at any time. Any residues of a releasable layer of oxide, for example, may then be removed by applying a solution of hydrofluoric acid (HF).

The present invention may also be used to produce structures including low density insulating layers (oxide or nitride) having a low dielectric constant, or even a functionalization as indicated above. The microcavities contribute to reducing the mean density of the insulating layer and they enclose an atmosphere having a low electric value. This thereby reduces the coupling between the wafers, limiting the permittivity of the insulating layer.

Further, the microcavities may be functionalized, in particular by doping. Thus, by introducing nitrogen during the thermochemical oxidation treatment, for example, the nitrogen is caused to migrate to the interfaces of the cavities and create negative charges therein.

In general, it is possible to introduce different species into the cavities, in particular metals, by doping during the thermochemical oxidation or nitriding treatment. By introducing conductive materials into the cavities, it is possible to produce buried layers of oxide or nitride that are electrically charged. It is also possible to form layers comprising isolated electrodes, for example floating gates, by

functionalizing the cavities by introducing species forming conductive or semiconductive materials.

Doping and/or functionalizing the cavities may in particular be carried out after oxidation/nitriding ("post-ox", "post-nitride") or during oxidation/nitriding per se, using one of the following techniques:

- implantation;
- annealing after oxidation/nitriding, in an atmosphere comprising specific gases or precursors that, for example, allow diffusion of active species;
- plasma.

The species used during doping and/or functionalization may be selected from at least one of the following species:

- nitrogen (charges on the surface of the cavities);
- dopants such as boron, arsenic, phosphorus, antimony, aluminum, gallium, etc, in particular in order to modify the band diagram of a semiconductor;
- metals such as iron, nickel, cobalt, etc, which modify the electrical properties by migrating towards the surface of the cavities.

Any other material that can functionalize the cavities may be envisaged.

The cavities present in the oxide or nitride layer may also act as traps for contaminating species that may cause electrical disturbances. By trapping this type of species in the cavities in the buried layer of oxide or nitride, i.e. far from the interfaces with the useful layers present above the oxide or nitride catalytic, the quality and the electrical properties of the useful layers are improved.

The cavities in the layer of oxide or nitride may also act as traps for hydrogen atoms. Under such circumstance, the cavities greatly increase the hydrogen storage capacity of the layer of oxide or nitride, in particular when it is thin. The solubility of hydrogen in an oxide or a nitride is very low and the presence of

cavities means that the capacity to retain hydrogen trapped thereby is increased. During bonding of a substrate to the structure of the invention, trapping and conservation of hydrogen in the layer of oxide or nitride including microcavities means that it is possible to avoid re-opening the bonding interface between these two elements during heat treatments, in particular during heat treatments for consolidation of the bonding interface. Cavities are also formed at the bonding interface and may be placed under pressure using hydrogen that diffuses from the structure. By retaining the hydrogen at the layer of oxide or nitride, it cannot reach the cavities present at the bonding interface, which thus ensures good bonding integrity.

Figure 7 illustrates a composite structure 200 produced in accordance with the method of the invention. The composite structure 200 is a silicon substrate including an insulating $SiO_2$ layer 205 formed by surface oxidation of the substrate. The composite structure 200 also includes a layer of silicon 206 corresponding to the non-oxidized portion of the silicon substrate. The structure also includes a buried layer of microcavities 203 that is present in its entirety in the insulating layer 205. In accordance with the invention, this layer of microcavities is formed by ion implantation and heat treatment of the substrate before the formation of the insulating layer under conditions similar to those described above. As explained above, the formation of the insulating layer 205 does not cause the disappearance of cavities already formed in the substrate but modifies their shape. In fact, after the oxidation (or nitriding) front has passed into the layer of microcavities, the cavities all have a substantially oblong shape that is principally due to anisotropy of the rate of growth of the insulating layer during the oxidation/nitriding step.

Further, after the insulating layer has been formed in the layer of microcavities, the cavities with an

oblong shape are all oriented in the same direction as regards their length. In Figure 7, the microcavities 204 are all oriented with their lengths vertical. However, it is possible to obtain cavities with an oblong shape oriented in other directions, such as cavities that are parallel to the plane of the substrate or forming an angle therewith. The orientation of the cavities principally depends on the crystalline orientation presented by the substrate prior to the oxidation/nitriding step.

Obtaining a layer of cavities of oblong shape that are aligned with one another in an insulating layer has particular advantages. When the composite structure of the invention is used to form a structure that is releasable by mechanical fracture at the insulating layer including the cavities, said alignment of the cavities means that the process of fracture can be better controlled and a continuous and regular fracture line can be formed, meaning that the post-fracture roughness is thereby reduced. When the cavities are functionalized, for example by introducing electrical charges by doping the cavities, the alignment of the cavities means that the overall electrical properties of the layer can be adjusted.

CLAIMS

1. A method of producing a layer of cavities in a structure (100) comprising at least one substrate (101) formed from a material that can be oxidized or nitrided, the method comprising the following steps:

• implanting ions (10) into said substrate (101) in order to form an implanted ion concentration zone (102) at a predetermined mean depth;

• heat treating the implanted substrate to form a layer of cavities (103) at the implanted ion concentration zone (102); and

• forming an insulating layer (105) in said substrate by thermochemical treatment from one surface of said substrate, said insulating layer that is formed extending at least partially into the layer of cavities (103).

2. A method according to claim 1, characterized in that the insulating layer (205) formed by thermochemical treatment extends over the entire layer of cavities (203).

3. A method according to claim 1 or claim 2, characterized in that the material of the substrate (101) is selected from at least the following materials: silicon, III/V materials, germanium and silicon-germanium, and silicon carbide.

4. A method according to any one of claims 1 to 3, characterized in that the thermochemical treatment of the substrate is carried out in an oxidizing atmosphere in order to form an insulating layer (105) of oxide.

5. A method according to any one of claims 1 to 3, characterized in that the thermochemical treatment of the substrate is carried out in a nitriding atmosphere in order to form an insulating layer of nitride.

6. A method according to claim 4, characterized in that the insulating oxide layer (105) extends into an upper portion of the layer of cavities (103), the lower portion of the layer of cavities being located in the non-oxidized silicon substrate, and in that the cavities (104a) present in the insulating oxide layer are substantially oblong in shape with a width in the range approximately 1 nm to 30 nm and with a length in the range 10 nm to 60 nm while the cavities (104b) present in the non-oxidized substrate have a diameter in the range 25 nm to 35 nm.

7. A method according to any one of claims 1 to 6, characterized in that one or more dopants are introduced into the substrate during the thermochemical treatment.

8. A method according to claim 7, characterized in that the dopant or dopants are selected from at least: nitrogen, boron, arsenic, phosphorus, antimony, aluminum, gallium, iron, nickel, and cobalt.

9. A method of producing a multilayer structure, comprising at least bonding a first structure onto a second structure, the second structure comprising a substrate including a layer of cavities and an insulating layer formed in accordance with a method according to any one of claims 1 to 8.

10. A method according to claim 9, characterized in that the first structure comprises a layer of semiconductor material and in that the multilayer structure is of the SeOI type.

11. A composite structure (200) comprising a substrate constituted by a material that is capable of being oxidized or nitrided, the structure further comprising an

insulating layer (205) formed by thermochemical treatment of the material of said substrate, said insulating layer including a layer of cavities (203), the structure being characterized in that the cavities (204) of said layer are oblong in shape and in that said cavities are oriented in the same direction.

12. A structure according to claim 11, characterized in that the substrate is selected from at least the following materials: silicon, III/V materials, germanium and silicon-germanium, and silicon carbide.

13. A structure according to claim 11 or claim 12, characterized in that the insulating layer (205) is a layer of oxide or nitride.

14. A structure according to any one of claims 11 to 13, characterized in that the cavities of said layer of cavities contain one or more dopants selected from at least: nitrogen, boron, arsenic, phosphorus, antimony, aluminum, gallium, iron, nickel, and cobalt.

15. A structure according to any one of claims 11 to 14, characterized in that the cavities (204) of said layer of cavities (203) have a width in the range approximately 1 nm to 30 nm and a length in the range 10 nm to 60 nm.