DESCRIPTION

TITLE: METHOD OF MANUFACTURING A FERROELECTRIC LAYER TRANSFERRED ONTO A SUBSTRATE AND OF POLARIZATION WITH IMPROVED HOMOGENEITY

TECHNICAL FIELD OF THE INVENTION

[0001] The invention relates to a method of manufacturing a ferroelectric layer transferred onto a substrate and of polarization with improved homogeneity in its thickness. Such a structure can be used to form, for example, radio frequency (RF) components, in particular elastic wave components, in particular surface acoustic wave (SAW) or bulk acoustic wave (BAW) components.

TECHNOLOGICAL BACKGROUND

[0002] There are several types of applications that take advantage of, or are influenced by, the polarization properties of ferroelectric materials and the presence of domains with polarizations opposite to each other. These include electroacoustic devices such as Surface Acoustic Wave (SAW) devices or Bulk Acoustic Wave (BAW) devices. The existence of such applications has led to the development of methods of controlling the polarization domains of ferroelectric layers.

[0003] The article ""Seeing Is Believing"-In-Depth Analysis by Co-Imaging of Periodically-Poled X-Cut Lithium Niobate Thin Films", by Sven Reitzig et al., published in Crystals 2021, 11, 288, describes a lithium niobate layer integrated on a silicon substrate via a silica layer, and the control of the polarization of this layer parallel to the plane wherein it extends, by applying a voltage between electrodes arranged periodically on the free surface of the layer. It should be noted that, in such a structure comprising electrodes only on the free face of the crystal, the control of a polarization that would be

perpendicular to the substrate by means of an electric field, in the absence of a buried electrode, would require voltages risking the breakdown of the silica layer.

[0004] Document EP 0 592 226 A1 describes an optical frequency conversion device obtained by the periodic juxtaposition of parallel bands of reversed polarization at one face of a ferroelectric substrate exhibiting spontaneous polarization perpendicular to the plane of extension of the substrate, that is perpendicular to this face. The reversal of polarization along the bands is achieved by proton exchange through a mask.

[0005] Document WO 2005/052682 A1 discloses the localized polarization reversal of a ferroelectric crystal with spontaneous polarization perpendicular to one of its faces, by applying an electric field along juxtaposed periodic bands, by means of gel electrodes arranged on this face and the opposite face of the crystal.

[0006] The structures and methods presented hereinbefore, while they do actually allow the polarization domains of a ferroelectric layer to be controlled at its surface, remain impractical and do not allow polarization to be controlled through the thickness of this layer or its integration on a support.

[0007] In response to these shortcomings, the international patent application with publication number WO 2020/200986 A1 and the French patent applications with filing numbers FR2301220 and FR2301221 propose techniques for transferring ferroelectric layers onto a substrate. However, these techniques do not solve the problem completely satisfactorily, in that, at the end of manufacture, the transferred ferroelectric layers may exhibit uncontrolled polarization inhomogeneities in the thickness of the layer, in particular with regard to the transfer of ferroelectric layers having negative polarization onto the final support substrate.

DISCLOSURE OF THE INVENTION

[0008] One object of the invention is to provide a method of manufacturing a ferroelectric layer transferred onto a substrate, the method correcting or preventing any polarization inhomogeneities that might appear in their thickness, in particular for the situation where a ferroelectric layer of negative polarization is sought, that is, oriented towards the support of the ferroelectric layer.

[0009] In order to produce these objects, one aspect of the invention is a method of manufacturing a structure comprising a ferroelectric layer of negative polarization, comprising the steps of: providing a wafer of ferroelectric material having a first face and exhibiting polarization oriented towards this face; forming an embrittlement plane in the wafer of ferroelectric material by implanting hydrogen ions through the first face; assembling the wafer of ferroelectric material comprising the embrittlement plane to a support assembly by bringing the first face into contact with a free surface of the support assembly; detaching a part of the wafer of ferroelectric material so as to define a ferroelectric layer detached from the wafer of ferroelectric material and assembled to the support assembly so as to obtain a structure formed of the ferroelectric layer and of the support assembly, the ferroelectric layer exhibiting negative polarization; carrying out an additional full-field hydrogen implantation step, configured so as to correct or to prevent the occurrence of polarization reversal in the volume of the ferroelectric layer and/or at its interface with the support assembly; and applying at least a first heat treatment to the structure.

[0010] An advantage of the method according to the invention is its ability to produce a structure including a ferroelectric layer transferred onto a substrate and with negative polarization, oriented towards the interface between the ferroelectric layer and its support, exhibiting improved homogeneity over its thickness compared to known manufacturing methods. Such a structure facilitates, for example, the integration of bulk acoustic functions while maintaining a low cost and enabling a high level of performance.

[0011] According to additional non-limiting features of the invention, considered either individually or in any technically feasible combination:

- the additional hydrogen implantation step can be carried out after the at least one first heat treatment, the method further comprising a step of applying a second heat treatment to the structure after the additional hydrogen implantation step;
- the method may further comprise a step of thinning the ferroelectric layer, preferentially between the step of applying the first heat treatment and the step of applying the second heat treatment;
- the additional hydrogen implantation step can be performed prior to the at least first heat treatment;
- the method may further comprise a step of thinning the ferroelectric layer, preferentially after the step of applying the first heat treatment;
- the method may comprise a step of characterizing a reference structure, whereby an adjustment of parameters of the additional hydrogen implantation step can be defined in response to this characterization;
- the additional hydrogen ion implantation step may comprise a first correction ion implantation in the ferroelectric layer, configured so as to generate a projected path of the implanted hydrogen ions such that a depth of its maximum reaches or exceeds an interface depth between (i) a volume of stable polarization of the ferroelectric layer and (ii) a volume of reversed polarization due to the formation of the plane of embrittlement or of polarization that would reverse due to the formation of the embrittlement plane if a heat treatment were applied;
- the additional hydrogen ion implantation step may comprise a second correction ion implantation, configured so as to generate a projected path of implanted hydrogen ions such that a depth of its maximum reaches or exceeds the depth of the interface between (i) the ferroelectric layer and (ii) the support assembly, preferably at a distance from this interface which is less than the thickness of a polarization volume which is bounded by this interface and which is multi-domain or reversed with respect to a polarization of a stable

polarization volume of the ferroelectric layer or which would reverse or become multi-domain if a heat treatment were applied;

- the additional full-field hydrogen implantation step can be configured so as to obtain a hydrogen concentration of between 10^{19} and 10^{22} at/cm^3 in a volume of the structure;

- the ferroelectric layer can extend in an extension plane and the polarization makes an angle with it within an angular range of -20° to -160° with respect to the extension plane;

- the ferroelectric layer can be a layer of lithium niobate or of lithium tantalate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Other features and advantages of the invention will emerge from the following detailed description of the invention with reference to the appended figures, in which:

[Fig. 1] Figure 1 shows crystal cross-sections of single crystals;

[Fig. 2] Figure 2 shows the manufacture of a structure comprising a ferroelectric layer transferred onto a support;

[Fig. 3] Figure 3 shows the influence of the manufacture in Figure 2 on the polarization of the transferred ferroelectric layer;

[Fig. 4] Figure 4 shows a polarization reversal mechanism in a layer of ferroelectric material;

[Fig. 5] Figure 5 shows a method of correcting the polarization of a ferroelectric material by means of a first ion implantation;

[Fig. 6] Figure 6 shows a method of correcting the polarization of a ferroelectric material by means of a second ion implantation;

[Fig. 7] Figure 7 shows a structure comprising a transferred ferroelectric polarization layer with improved homogeneity;

[Fig. 8] Figure 8 shows a first manufacturing method according to the invention;

[Fig. 9] Figure 9 shows negative orientation polarization; and

[Fig. 10] Figure 10 shows a second manufacturing method according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

First embodiment of the invention

[0013] Depending on the piezoelectric device to be produced, an orientation must be selected for the polarization of the active layer of piezoelectric material, which consists of a layer of single-crystal ferroelectric material.

[0014] This ferroelectric material can be obtained by crystal growth using the so-called "Czochralski" method which produces a solid single crystal material in the form of an elongated cylinder known as a "ball" or "ingot" by pulling a seed crystal of chosen orientation bathed in a molten material corresponding to the crystal to be formed, along a pulling direction. The single crystal grows in this pulling direction. Wafers of the ferroelectric material are then obtained by cutting the ingot at a specific angle with respect to its direction of growth, then prepared and integrated as a ferroelectric layer in, for example, a piezoelectric device.

[0015] The orientation of the polarization of the layer depends on the crystal orientation of the cut wafer which, in the general case, does not correspond to the direction of growth of the single crystal. Of course, the person skilled in the art will know how to select the most appropriate seed close to the desired crystal orientation for ingot pulling in order to reduce material losses during cutting and machining into circular wafers.

[0016] Figure 1 shows at (A) and (B) the orientations of $LiTaO_3$ layers designated 42RY and -138RY, respectively. These names derive from the crystallographic orientation of these layers, corresponding to respective rotations of 42° and -138° of the y and z axes with respect to the trigonometric direction around the x axis to give the x', y' and z' axes, the x, y and z axes corresponding to the crystallographic axes specific to the single crystal and the y' axis being aligned with the direction normal to the cut and machined surface.

More specifically, the x, y and z axes correspond to axes $[\bar{1}\bar{1}20]$, $[01\bar{1}0]$, and $[0001]$, respectively.

[0017] After pulling in a chosen direction, it is known to the person skilled in the art to carry out polarization by applying an electric field in the z direction when the temperature falls below the Curie temperature in order to determine the direction of polarization.

[0018] Conventionally, a so-called negative polarization is a polarization with an orientation directed towards the interior of the material or of the structure concerned, or in other words, the projection of the z axis onto the y' axis is negative.

[0019] Conventionally, for a ferroelectric layer bonded to a substrate, a layer whose polarization orientation is directed towards the free surface of the layer is referred to as a positive polarization layer.

[0020] Conversely, still for a ferroelectric layer bonded to a substrate, a layer whose polarization orientation is directed inwardly, that is, towards the interface between the layer and its support, is referred to as a negative polarization layer.

[0021] Figure (2) shows at (D) a situation in which the polarization P1 of a ferroelectric layer $Ferro_{lay}$ is negative: it is oriented towards the interface between the ferroelectric layer P1 and the assembly supporting it, the latter herein consisting of an intermediate layer Int on a support layer Sprt. It can also be said that the polarization component along the vertical direction Vert perpendicular to the ferroelectric layer and oriented from the support assembly towards the ferroelectric layer, is negative. This component is obtained by a normal projection of the polarization on the Vert direction.

[0022] To obtain a piezoelectric device equipped, for example, with a ferroelectric layer of negative polarization, the characteristics of the wafer of

ferroelectric material used to manufacture the device must be selected in advance, and the manufacturing method and its potential impacts on the polarization of the wafer must be taken into account.

[0023] Figure 2 shows the general principle of a method of manufacturing the structure Struct shown in (D), which includes a step of transferring a ferroelectric layer $Ferro_{lay}$ onto a support assembly Sprt.Set formed of the intermediate layer Int on the support layer Sprt, the intermediate layer being interposed between the ferroelectric layer $Ferro_{lay}$ and the support layer. In a non-limiting manner, a layer of another material, in particular a silicon oxide layer, can also be found on the face of the ferroelectric layer $Ferro_{lay}$ before being arranged on the intermediate layer Int. The structure Struct is for example designed to be integrated into an electroacoustic device.

[0024] The characteristics of the support assembly can affect the acoustic properties of the layer $Ferro_{lay}$, which is important in the case of a structure forming part of an acoustic device. The nature and the thickness of these layers can therefore also be decisive for carrying out the desired processing of an electrical signal, or at least influencing this processing. In the example shown in Figure 2, the support assembly may comprise the support layer Sprt, and the intermediate dielectric assembly layer Int, preferably comprising an oxide, directly in contact with the ferroelectric thin layer $Ferro_{lay}$.

[0025] For reasons of availability and cost, the support layer Sprt can be made of silicon. This may be a support consisting of a solid base substrate of monocrystalline silicon, but the invention is not limited to this support, which may, more generally, be made of any material, for example silicon, even electrically insulating material such as sapphire or glass. The support layer Sprt, when it is formed of a solid substrate, is typically several hundred microns thick. It is possible to limit the density of electric charges, holes or electrons, which are likely to move in the support layer and which could affect the correct operation of an RF component formed on the basis of the structure Struct. The

support layer Sprt can thus consist of a high-resistivity silicon substrate, that is, having a resistivity greater than 1000 ohm-centimeter, and more preferentially still greater than 3000 ohm-centimeter. To reinforce the resistive nature of the support layer Sprt, the support layer Sprt can be provided with a charge trapping layer on the side of the ferroelectric layer, for example formed of polycrystalline silicon. Of course, it is possible for this charge trapping layer to be formed using a technique other than that of providing a layer formed of polycrystalline silicon. This layer may also comprise carbon or consist of or comprise silicon carbide or an alloy of silicon and carbon. Alternatively, it may be a matter of producing the electrical traps by ion bombardment of relatively heavy species (for example argon) in a surface part of the support layer in order to create crystal defects therein that are capable of trapping electric charges. It is also possible to provide a charge trapping layer formed of a porous material, for example by porosification of a surface part of the support layer Sprt when the latter is made of silicon. But the invention is not limited to a support layer exhibiting such characteristics.

[0026] By way of example, the intermediate layer Int may be made of silicon oxide, silicon nitride, or be formed of a stack of layers composed of these materials.

[0027] Alternatively, the intermediate layer may be an electrically conductive metal layer interposed between the ferroelectric layer $Ferro_{lay}$ and the support layer Sprt. In this example, the metal layer Int is in direct contact with each of the support Sprt and of the ferroelectric layer $Ferro_{lay}$. In this case, the layer Int can subsequently be used as a buried electrode intended to apply an electric field to the ferroelectric layer $Ferro_{lay}$.

[0028] The presence of an intermediate layer Int is just one option. Not all applications require the presence of such a layer.

[0029] Conventionally, the structure Struct may take the form of a circular wafer with a diameter of 100, 200, 300 or even 450 mm, but the invention is by no means limited to these dimensions or to this shape.

[0030] The ferroelectric layer $Ferro_{lay}$ may consist of a single-crystal ferroelectric material, such as lithium tantalate $LiTaO_3$ or lithium niobate LiNbO3, or else materials such as $BaTiO_3$, $PbZrTiO_3$, $KNbO_3$, $BaZrO_3$, $PbTiO_3$ or $KTaO_3$. These materials also exhibit piezoelectric properties. Generally speaking, the ferroelectric layer can have a thickness of between 10 nanometers and 10 microns, depending on the intended application of the structure Struct and the expected performance of the components, but the invention does not rule out the use of different thicknesses, again depending on the intended application. It is noted that a ferroelectric material is a material that has electric polarization in the natural state; polarization which can be reversed by applying an external electric field greater than the coercive field of the material. As shown in the present document, the ferroelectric layer preferably has single domain polarization, that is, that all dipole moments are aligned parallel to each other in a given direction. Herein, the given direction is inclined with respect to the plane of the ferroelectric layer, that is, inclined with respect to the free face of this layer.

[0031] With reference to Figures 2 to 9, the structure Struct can be produced by a manufacturing method 100 by transferring a ferroelectric layer onto a support assembly, the state method being summarized by Figure 8 and comprising:

- a step S00 of selecting and supplying a wafer of single-crystal ferroelectric material for its chemical composition and its crystal orientation with respect to its plane of extension, in order to serve as a ferroelectric donor substrate $Ferro_{sub}$, the selected wafer exhibiting a single-domain positive polarization - P1, that is, having a component oriented in the direction of its face designated by Top, that is, that the wafer has a crystal orientation between 0RY and 180RY, as shown in (B) of Figure 2;

- a step S10 of preparing a support assembly Sprt.Ens, herein consisting of a support layer Sprt provided with an intermediate layer Int on its surface as shown in (A) of Figure 2;

- a step S20 of preparing the ferroelectric donor substrate $Ferro_{sub}$ in order to form an embrittlement plane Frgl therein with a view to separating a ferroelectric layer $Ferro_{lay}$ from the donor substrate $Ferro_{sub}$ in a subsequent step, as shown in (B), the depth of the embrittlement plane Fgrl in the donor substrate $Ferro_{sub}$ defining the thickness of the ferroelectric layer $Ferro_{lay}$;

- a step S40 of assembling the support assembly Sprt.Ens with the donor substrate $Ferro_{sub}$, by bringing the free face Fr.Fac of the intermediate layer Int in contact with the face Top of the ferroelectric donor substrate $Ferro_{sub}$ in order to form an intermediate structure $Struct_{inter}$ shown in (C), with the intermediate layer Int interposed between the support layer Sprt and the face Top of the ferroelectric donor substrate $Ferro_{sub}$, the orientation of the polarity of the layer $Ferro_{lay}$ with respect to the support layer is reversed, from -P1 to P1 as a result of the turning over of the donor substrate $Ferro_{sub}$ for assembly; and

- a step S60 of detaching a part of the donor substrate $Ferro_{sub}$ from the intermediate structure at the embrittlement plane, leaving the ferroelectric layer $Ferro_{lay}$ bonded to the support Sprt and making it possible to obtain the structure Struct shown in (D), the ferroelectric layer $Ferro_{lay}$ having, as already mentioned, a negative polarization with respect to the normal Vert of the free surface used as the detachment interface.

[0032] The donor substrate $Ferro_{sub}$ shown in (B) is a substrate consisting of the ferroelectric material of the ferroelectric layer $Ferro_{lay}$. Alternatively, it could comprise a surface thickness of this material. Thus, the donor substrate can, as an example, be formed of a solid substrate of lithium tantalate or lithium niobate, or else a composite substrate formed of a first substrate on which a thickness (at least equal to that of the layer $Ferro_{lay}$) of lithium tantalate or lithium niobate is applied. The use of a composite substrate comprising a support substrate and a layer of ferroelectric material is necessary if the difference in the coefficient of thermal expansion of the ferroelectric material

and of the final substrate is too great to enable the Smart Cut process to be applied. This approach is described in detail in documents WO2019002080 and WO2019186032, which are incorporated by reference.

[0033] The donor substrate therefore comprises at least one layer of ferroelectric material having a first single-domain positive polarization -P1 inclined with respect to the plane of extension of the ferroelectric layer $Ferro_{lay}$ which depends on the chosen crystal orientation of the wafer. This layer is intended to be bonded to the intermediate layer Int before being separated from the donor substrate. In a non-limiting manner, a layer of another material, in particular a silicon oxide layer, can also be found on the face of the ferroelectric layer $Ferro_{lay}$ before being arranged on the intermediate layer Int.

[0034] Figure 2 shows a situation wherein the ferroelectric layer comes from a 42RY-type cut of $LiTaO_3$, with the orientation shown in (A) of Figure 1. The polarization of the layer is oriented upwards in (B) of Figure 2 as in (A) of Figure 1.

[0035] More generally, the method 100 applies to a crystal cut in the range extending from 0RY to 180RY, preferably 20RY to 160RY, for the donor substrate $Ferro_{sub}$. The polarization of the final structure is therefore negative, that is, oriented from 0° to -180°, preferably within an angular range [Ang] from -20° to -160°, with respect to the plane of the ferroelectric layer $Ferro_{lay}$, as shown in Figure 9.

[0036] The ferroelectric layer $Ferro_{lay}$ can be transferred from the ferroelectric donor substrate $Ferro_{sub}$ using Smart Cut™ technology, in which case the donor substrate must be prepared by introducing light species such as hydrogen and/or helium into this donor substrate. This introduction may correspond to an implantation of hydrogen, that is, an ion bombardment of hydrogen of the planar face Top of the donor substrate $Ferro_{sub}$. In a manner known per se, and as shown in (B), the implanted hydrogen ions H^+ are intended to form an embrittlement

plane Frgl delimiting the ferroelectric layer $Ferro_{lay}$ of ferroelectric material to be transferred which is located on the side of the face Top and another part $Ferro_{sep}$ forming the rest of the substrate and which will be separated from the ferroelectric layer $Ferro_{lay}$ in a subsequent step.

[0037] The nature, the dose of the implanted species, and the implantation energy are selected based on the thickness of the layer that is intended to be transferred and on the physico-chemical properties of the donor substrate $Ferro_{sub}$. In the case of a donor substrate made from $LiTaO_3$, it will be possible to choose to implant a hydrogen dose of between 10^{16} and 5.10^{17} at/cm² with energy that is between 30 and 300 keV to delimit a ferroelectric layer $Ferro_{lay}$ of the order of 200 to 2000 nm thick.

[0038] In (C) of Figure 2, polarization P1 is oriented towards the interface between the ferroelectric layer $Ferro_{lay}$ and the intermediate layer Int, so that the polarization of the ferroelectric layer is considered negative.

[0039] The support substrate Sprt may have the same dimension and the same shape as that of the donor substrate $Ferro_{sub}$, but the invention is not limited to such a configuration and different dimensions, shapes and configurations may be employed. Prior to assembly, it is possible to contemplate preparing the faces of the substrates to be assembled using a cleaning, brushing, drying or polishing step, or using plasma activation, or else before or after cleaning a deposition of a bonding layer.

[0040] The assembly may correspond to the placing of the donor substrate $Ferro_{sub}$ in close contact with the support Sprt by molecular adhesion and/or electrostatic bonding.

[0041] As is well known, during a molecular adhesion method, the exposed surfaces of the support Sprt and of the donor substrate $Ferro_{sub}$, which are perfectly clean, flat and smooth, are placed in close contact to promote

electrostatic bonding or the development of molecular bonds, for example of the van der Waals or covalent type. The two bodies are then assembled without the use of adhesives.

[0042] The assembly may comprise the application of low-temperature heat treatment (for example, between 50 and 300°C, typically 100°C) allowing the crystal defects present in the ferroelectric layer to be healed and to sufficiently strengthen the bonding energy to allow any subsequent thinning step.

[0043] In the present embodiment, the step of detaching a part of the donor substrate is performed by applying Smart Cut™ technology, according to which a layer intended to form the ferroelectric layer $Ferro_{lay}$ is delimited by the embrittlement plane Frgl defined by implanting hydrogen ions in the donor substrate, as shown in (B) of Figure 2. After the assembly step, this layer is detached from the donor substrate by fracture at the embrittlement plane Frgl and thus transferred onto the support Sprt, as shown in (D) of Figure 2.

[0044] This detachment step may thus comprise applying to the intermediate structure $Struct_{inter}$ a heat treatment in a temperature range of the order of 80°C to 300°C to enable detachment of the part of the donor substrate from the ferroelectric layer $Ferro_{lay}$ and thus complete transfer thereof onto the support assembly. In place of or in addition to the heat treatment, this step may comprise the application of a blade or a jet of gaseous or liquid fluid, or any other force of a mechanical nature at the embrittlement plane Frgl.

[0045] Following step S60 which produces the structure shown in (D) of Figure 2 by separating the layer $Ferro_{lay}$ from the rest of the donor substrate $Ferro_{sub}$, a stabilizing heat treatment H.Treat-1 is applied to the structure Struct in step S80. The stabilizing heat treatment heals crystal defects present in the ferroelectric layer and helps consolidate the bond between this ferroelectric layer $Ferro_{lay}$ and the intermediate layer Int. In the case of LiTaO3, this heat treatment is intended to bring the ferroelectric layer to a temperature between

300°C and the Curie temperature of the ferroelectric material (and preferentially greater than or equal to 450°C, 500°, 550° or up to 600°) for a period of between 5 minutes and 10 hours. This heat treatment is preferentially carried out by exposing the free face of the dielectric layer to an oxidizing or neutral gaseous atmosphere.

[0046] However, the inventors have found that the heat treatment H.Treat-1, combined with the previous manufacturing steps and with the structure Struct itself, has several effects that locally modify the polarization of the layer $Ferro_{lay}$, as explained with the help of Figure 3.

[0047] One of these effects is particularly troublesome, modifying the polarization of the core of the layer $Ferro_{lay}$, that is, a part of the layer located at a distance from its surface or from its interface with the support assembly. Indeed, the presence of a hydrogen ion concentration gradient in a ferroelectric layer combined with a heat treatment at a temperature in the range of 300° to 600°C, such as heat treatment H.Treat-1, causes a reversal of the polarization of the ferroelectric material in the volume where the gradient is sufficiently strong. It is interpreted that the gradient of implanted H+ ions causes the appearance of an electric field E_H which, thanks to the thermal activation caused by the rise in temperature, can induce the reversal of polarization in a volume of the material. More specifically, when heat-treated at a sufficiently high temperature, the polarization of the ferroelectric material tends to take on the same orientation as the field E_H, thus reversing the polarization when E_H is oriented in a direction opposite to that of the material prior to application of the heat treatment.

[0048] Figure 3 shows in four lines, Lin.A to Lin.D, the impact of the heat treatment H.Treat-1 in step S80 on the polarization in the volume of the layer $Ferro_{lay}$, in conjunction with certain manufacturing steps. Each line corresponds to a manufacturing step and is divided into two columns. A first column, Col.1, shows the polarization of the layer $Ferro_{lay}$ in the absence of heat treatment and corresponds to the manufacturing steps shown in Figure 2, while a second

column, Col.2, shows the effects caused by these different steps when heat treatment is applied in step S80. Particular attention will be paid to the appearance and evolution of distinctly polarized volumes in the layer $Ferro_{lay}$.

[0049] Line Lin.A shows the ferroelectric donor substrate $Ferro_{sub}$ in step S00. Its polarization is indicated by -P1 because it is opposite in direction to the polarization P1 of the final structure Struct to be obtained, shown in (D) of Figure 2. This polarization is homogeneous throughout the volume V_B which, at this point, is defined by the volume of the entire donor substrate $Ferro_{sub}$. The two columns, Col.1 and Col.2, show no difference: in the absence of hydrogen ions implanted according to an inhomogeneous profile in the volume V_B of $Ferro_{sub}$, heat treatment does not cause polarization reversal.

[0050] Line Lin.B shows the state of the donor substrate $Ferro_{sub}$ after formation of the embrittlement plane Frgl in step S20. Without heat treatment (see Col.1), the polarization of the donor substrate remains unchanged. On the other hand, following heat treatment, or if heat treatment were applied immediately without carrying out steps S40 and S60, polarization would be reversed in a material volume V_C derived from material volume V_B, in the vicinity of the embrittlement plane Frgl. The polarization of volume V_C then corresponds to that of a -138RY cut of ferroelectric material $LiTaO_3$, as shown by the number -138 on the figure. Outside the volume V_c, polarization remains unchanged.

[0051] This mechanism is shown in Figure 4, which shows the distribution of hydrogen ions implanted in the layer $Ferro_{lay}$ as a concentration of hydrogen [H] according to the implantation depth Dpth from the surface of the layer $Ferro_{lay}$ (also referred to as a "projected path" in the field of ion implantation). Such a distribution, which is highly inhomogeneous depending on the depth of the layer $Ferro_{lay}$, generates the electric field E_H, which can lead to polarization reversal of the volume concerned when heat treatment is applied at a sufficiently high temperature. In fact, under these conditions, polarization tends to take on the same orientation as the electric field E_H. Herein, part of the volume V_B,

influenced by the hydrogen ion concentration gradient and the electric field it generates, has seen its polarization reversed from P1 to -P1 in the volume V_C.

[0052] Line Lin.C shows the state of the donor substrate following its assembly to the support assembly in step S40. To do this, the donor substrate is turned over. By symmetry, we find ourselves in the situation we would have if we had used a -138RY cut of ferroelectric material $LiTaO_3$ as a substrate $Ferro_{sub}$ without having turned it over during assembly. In practice, the polarizations of the two volumes V_B and V_C are reversed, as shown by the polarization arrows P1 and -P1 and by the indications 42 and -138 corresponding to the 42RY and -138RY cuts.

[0053] Line Lin.D shows, in addition to the presence of two volumes V_B and V_C already described, the presence of two other volumes V_A and V_D of reversed polarizations, respectively originating from volumes V_B and V_C following the heat treatment in step S80. These two volumes appear on both sides of the layer $Ferro_{lay}$. The volume V_D is defined by a part of the volume V_C as defined in line Lin.C, whose polarization is partially or totally reversed at the free surface of the layer $Ferro_{lay}$. Volume V_A is defined by a part of volume V_B as defined in line Lin.C, whose polarization reverses partially or totally at the interface of the layer $Ferro_{lay}$ with the support assembly, and therefore with the layer Int of this example. These reversals of polarities occur as a result of surface and interface physico-chemical interactions related to the temperature of the heat treatment applied, and cause the transformation of surface portions of this ferroelectric layer from a single-domain ferroelectric structure of a first polarization to a ferroelectric structure of a second polarization opposite to the first polarization, or to a multi-domain ferroelectric structure at its free surface and/or at its interface with the support assembly. These surface portions are said to be multi-domain when they have a ferroelectric structure exhibiting zones of different polarization orientations. These surface portions are typically of the order of 150 nm thick or less, and can develop over the entire extent of the ferroelectric layer.

[0054] We can see that the manufacturing method of the structure Struct should preferably take into account the formation of volumes V_A, V_C and V_D from volume V_B, to improve the polarization homogeneity of the ferroelectric layer $Ferro_{lay}$, which is inhomogeneous in depth, and therefore leads to poorly controlled characteristics for devices incorporating this layer. The part of volume V_B not undergoing polarization reversal is considered to be a stable polarization volume of the ferroelectric layer $Ferro_{lay}$.

[0055] Volume V_D can simply be removed by polishing the surface of the layer $Ferro_{lay}$.

[0056] In a step S100 following step S80, during which the heat treatment is applied, the ferroelectric layer is thinned. This thinning can correspond to polishing of the free face of the ferroelectric layer $Ferro_{lay}$, for example by mechanical, chemical-mechanical thinning techniques and/or chemical etching. It enables the free face to be prepared so that it exhibits low roughness, for example less than 0.5 nm RMS 5×5 µm by atomic force microscopy (AFM) and so that the volume V_D of the ferroelectric layer $Ferro_{lay}$ is removed. A removal of 50 to 300 nm of thickness is generally provided in order to reach the target thickness of the ferroelectric layer $Ferro_{lay}$, and in all cases a thickness greater than that of volume V_D. The polarization homogeneity of the layer $Ferro_{lay}$ is thus improved.

[0057] In order to improve the polarization homogeneity of the layer $Ferro_{lay}$ in depth, it is proposed to proceed, after step S100, with a step S120 of implanting Corr.Imp correction hydrogen ions in the thickness of the structure Struct followed by a second heat treatment H.Treat-2 in step S140, so as to correct the polarization of volumes V_A and V_C. Step S120 may optionally comprise several ion implantation phases, but must comprise at least one thereof. Of course, in other embodiments, and without limiting the invention, it is also possible to carry out the step S120 of implanting Corr.Imp correction hydrogen ions prior to said thinning step S100.

[0058] Figure 5 shows a first correction ion implantation leading to a projected path R_P of the implanted hydrogen ions such that the depth $D1(R_P)$ of its maximum reaches or exceeds the depth of the interface between volumes V_B and V_C and lies at or close to this interface in either volume V_C or in volume V_B, preferably at a predetermined distance such that the hydrogen concentration in volume V_C exceeds a threshold of 10^{19} hydrogen atoms per cubic centimeter, for example with a hydrogen concentration of between 10^{19} and 10^{22} atoms/cm^3 at a plane parallel to the free surface of the layer $Ferro_{lay}$. This first correction ion implantation will have a counteracting effect to that of the ion implantation that formed the embrittlement plane and will therefore correct the polarization of volume V_C again reversing its polarization and reorienting it like that of volume V_B.

[0059] Figure 6 shows a second correction ion implantation leading to a projected path R_P of the implanted hydrogen ions such that the depth $D2(R_P)$ of its maximum reaches or exceeds the depth of the interface between volume V_A and the layer Int, that is, the interface between the ferroelectric layer $Ferro_{lay}$ and the support assembly Sprt.Ens, and is located at this interface or in the layer Int, preferably at a predetermined distance such that the hydrogen concentration in volume V_A exceeds a threshold of 10^{19} hydrogen atoms per cubic centimeter, for example with a hydrogen concentration of between 10^{19} and 10^{22} atoms/cm^3 at a plane parallel to the free surface of the layer $Ferro_{lay}$. This second correction ion implantation, combined with the second heat treatment H.Treat-2, will have a counteracting effect to that of the physico-chemical effects occurring at the interface between V_A and Int, and will therefore correct the polarization of volume V_A by reversing its polarization again and reorienting it like that of volume V_B.

[0060] The first implantation and the second implantation are carried out "full field", that is, over the entire surface of layer $Ferro_{lay}$, with no masking to create implantation patterns in a useful area of the layer. However, a holding system

can be used to hold the structure in place during operation and mask certain parts of the layer $Ferro_{lay}$, in particular the periphery, these masked parts not being considered as part of the useful area of the structure Struct. Implantation energies of between 30 keV and 300 keV, and doses of between 1.10^{15} and 9.10^{16} atoms/cm^2 can be considered.

[0061] Depending on the characteristics of the ferroelectric layer $Ferro_{lay}$, and in particular its thickness, the second implantation may be sufficient to correct the polarization orientations of the two volumes V_A and V_C. Indeed, the electric field generated by the hydrogen concentration gradient can be sufficiently extensive and intense to comprise volume V_C in its zone of influence and influence polarization during heat treatment H.Treat-2. It is then understood that a relatively thin ferroelectric layer is more likely to benefit from this advantage than a relatively thick ferroelectric layer.

[0062] The first correction implantation and the second correction implantation can be carried out successively during correction step S120. Alternatively, the first implantation or the second implantation can be performed alone.

[0063] The implantation parameters of correction step S120 are preferably adjusted based on the geometric characteristics (thickness, location) of volumes V_A and V_C of the layer $Ferro_{lay}$. To this end, a first preparatory step Prep-S00 consists of manufacturing a reference structure Ref according to the same parameters as the structure Struct to be produced, therefore according to steps S00 to S100.

[0064] A second preparatory step Prep-S10 consists in performing a polarization analysis along a transverse plane of the layer $Ferro_{lay}$ of the reference sample, in order to obtain the polarization characteristics Char of the sample Ref. To achieve this, a bevel cut is made in the layer $Ferro_{lay}$ then this cut is analyzed using piezoresponse force microscopy (PFM). Such an analysis makes it possible to determine the polarization orientation of the layer $Ferro_{lay}$ throughout its entire

thickness, and therefore to determine the absence or the presence of reverse polarization volumes and, where applicable, to locate volumes V_A, V_B, V_C and V_D, that is, the thicknesses of each of these volumes and therefore the depths at which the interfaces between V_A and V_B, V_B and V_C, and V_C and V_D are located, measured from the free surface of the layer $Ferro_{lay}$.

[0065] Step S120 can be applied with implantation parameters adjusted in response to the analysis performed in step Prep-S10. Specifically, the implantation energy of the first ion implantation will be determined in a manner such that the depth D1(R_P) of the maximum of the projected path R_P of hydrogen ions reaches or lies close to the depth of the interface between volumes V_B and V_C or else lies at this interface or even in volume V_c or in volume V_B, preferably at a predetermined distance already mentioned hereinbefore to exceed the concentration threshold. The same principle applies to the depth D2(R_P) of the second implantation, whose implantation energy will be determined in a manner such that the depth D2(R_P) of the maximum of the projected path R_P of the hydrogen ions reaches or lies close to the depth of the interface between volume V_A and the layer Int, or else lies at this interface, in volume V_A or even in the layer Int.

[0066] The second heat treatment H.Treat-2 of step S140, applied to the structure Struct after the step S120 of correction implantation Corr.Imp, can be intended to bring the ferroelectric layer to a temperature between 300°C and the Curie temperature of the ferroelectric material (and preferentially greater than or equal to 450°C, 500° or 550°, up to 600°) for a period of between 5 minutes and 10 hours. This heat treatment is preferentially carried out by exposing the free face of the dielectric layer to an oxidizing or neutral gaseous atmosphere. H.Treat-2 leads to a reversal of the polarization of volumes V_C and/or V_A and therefore to polarization homogenization of the ferroelectric layer $Ferro_{lay}$. Ideally, this layer is made, at the end of the treatment, of a single monodomain of negative polarization P1, oriented towards the interface

between the layer $Ferro_{lay}$ and the support assembly, herein comprising the intermediate layer Int and the support layer Sprt, as shown by Figure 7.

Second embodiment of the invention

[0067] According to the first embodiment of the invention, a hydrogen implantation step and an associated heat treatment are applied to correct the polarization of the ferroelectric layer in response to undesired polarization reversals, caused by a first heat treatment. This is a polarization repair process.

[0068] As an alternative to the first embodiment, the second embodiment prevents polarization reversals which, although undesired, can be expected.

[0069] Figure 10 shows a method 200 of manufacturing the structure Struct shown in Figure 2. Steps S00 to S60 are the same as those of method 100 in the first embodiment.

[0070] In the second embodiment, following detachment of the layer $Ferro_{lay}$ from the donor substrate $Ferro_{sub}$ in step S60, an ion implantation step S270 is carried out. This step is similar to step S120 in the first embodiment, with the slight difference that it is necessary to take into account the fact that the layer $Ferro_{lay}$ has not yet been thinned or has not yet been subjected to a heat treatment. The principle remains the same, however, and can be applied after the preparation and characterization steps of a reference sample Ref'.

[0071] The reference sample Ref' is a sample obtained in a step Prep-S00 by means of steps S00 to S60, further subjected to a step of applying a stabilizing heat treatment such as that of step S80 in the first embodiment. This heat treatment reveals the effects on the polarization of the layer $Ferro_{lay}$ of manufacturing steps S00 to S60, as explained hereinbefore, in particular in the comments with reference to Figure 3, concerning reversed polarization volumes. The analysis step Prep-S10 is used to obtain the characteristics

Char' of volumes V_A, V_B, V_C and V_D on the basis of which the implantation parameters of step S270 are selected, as in the first embodiment.

[0072] Following step S270, a heat treatment H.Treat' is applied to the structure Struct in step S280. The treatment H.Treat' replaces the two treatments H.Treat-1 and H.Treat-2 of the first embodiment, herein with a stabilizing effect on the structure Struct like treatment H.Treat-1. Step S270 results in the formation of hydrogen ion concentration gradients generating electric fields opposing polarization reversals in the volume of the ferroelectric layer. Thus, the polarization reversal volumes V_A and V_C of volume V_B in the first embodiment are not formed. Step S270 prevents polarization reversals that may occur in the volume of the ferroelectric layer, at the buried interface of the ferroelectric layer with the support assembly, or at these two regions.

[0073] However, the heat treatment H.Treat' can cause the appearance of a multi-domain volume on the surface of the layer $Ferro_{lay}$, as previously explained. Step S290, similar to step S100 in the first embodiment, is then required to remove the surface multi-domain layer and to bring the layer $Ferro_{lay}$ to the desired thickness.

[0074] Method 200 has the advantage over method 100 of being simpler, requiring only one heat treatment step instead of two.

[0075] The figures in this document are not necessarily to scale. Some characteristics and some components may be shown exaggerated with respect to other components or in somewhat schematic form, and some details of conventional elements may not be shown in the interests of clarity and conciseness.

[0076] Naturally, the invention is not limited to the embodiments described, and it is possible to add alternative embodiments without departing from the scope of the invention as defined by the claims.

Claims

1. A method of manufacturing a structure comprising a ferroelectric layer of negative polarization (P1), comprising the steps of:

- providing (S00) a wafer of ferroelectric material ($Ferro_{sub}$) having a first face (Top) and exhibiting a polarization (-P1) oriented towards this face;

- forming (S20) an embrittlement plane (Frgl) in the wafer of ferroelectric material ($Ferro_{sub}$) by implanting hydrogen ions through the first face (Top);

- assembling (S40) the wafer ($Ferro_{sub}$) of ferroelectric material comprising the embrittlement plane (Frgl) to a support assembly (Sprt.Set) by bringing the first face into contact with a free surface of the support assembly;

- detaching (S60) a part of the wafer of ferroelectric material so as to define a ferroelectric layer ($Ferro_{lay}$) detached from the wafer of ferroelectric material ($Ferro_{sub}$) and assembled to the support assembly (Sprt.Set) so as to obtain a structure (Struct) formed of the ferroelectric layer and of the support assembly, the ferroelectric layer exhibiting a negative polarization (P1);

- carrying out (S120; S270) an additional full-field hydrogen implantation step, configured so as to correct or to prevent the occurrence of polarization reversal in the volume of the ferroelectric layer and/or at its interface with the support assembly (Sprt.Ens); and

- applying (S80, S280) at least a first heat treatment (H.Treat-1; H. Treat') to the structure (Strct).

2. The method according to claim 1, wherein the additional hydrogen implantation step (S120) is carried out after the at least first heat treatment (S80, Htreat-1), the method further comprising a step (S140) of applying a second heat treatment (H.Treat-2) to the structure after the additional hydrogen implantation step (S120).

3. The method according to claim 2, further comprising a step (S100) of thinning (S.Pol) the ferroelectric layer, preferentially between the step (S80) of

applying the first heat treatment (H.Treat-1) and the step (S140) of applying the second heat treatment (H.Treat-2).

4. The method according to claim 1, wherein the additional hydrogen implantation step (S270) is carried out prior to the at least first heat treatment (S280, Htreat').

5. The method according to claim 4, further comprising a step (S290) of thinning (S.Pol') the ferroelectric layer, preferentially after the step (S280) of applying the first heat treatment (H.Treat').

6. The method according to any one of the preceding claims 1 to 5, comprising a step (Prep-S10) of characterizing a reference structure (Ref; Ref'), an adjustment of parameters of the additional hydrogen implantation step (S120; S270) being defined in response to this characterization.

7. The method according to any one of the preceding claims 1 to 6, wherein the additional hydrogen ion implantation step (S120; S270) comprises a first correction ion implantation into the ferroelectric layer ($Ferro_{lay}$), configured so as to generate a projected path of implanted hydrogen ions such that a depth ($D1(R_P)$) of its maximum reaches or exceeds an interface depth between (i) a volume (V_B) of stable polarization of the ferroelectric layer ($Ferro_{lay}$) and (ii) a volume (V_C) of reversed polarization due to the formation of the plane of embrittlement or of polarization that would reverse due to the formation of the embrittlement plane if a heat treatment were applied.

8. The method according to any one of the preceding claims 1 to 7, wherein the additional hydrogen ion implantation step (S120; S270) comprises a second correction ion implantation, configured so as to generate a projected path of implanted hydrogen ions such that a depth ($D2(R_P)$) of its maximum reaches or exceeds the depth of the interface between (i) the ferroelectric layer ($Ferro_{lay}$) and (ii) the support assembly (Sprt.Ens), preferably at a distance

from this interface which is less than the thickness of a volume (V_A) of polarization which is bounded by this interface and which is multi-domain or reversed with respect to a polarization of a volume (V_B) of stable polarization of the ferroelectric layer ($Ferro_{lay}$) or which would reverse or become multi-domain if a heat treatment were applied.

9. The method according to any one of the preceding claims 1 to 8, wherein the additional full-field hydrogen implantation step is configured so as to obtain a hydrogen concentration of between 10^{19} and 10^{22} at/cm^3 in a volume (V_A, V_B, V_C) of the structure.

10. The method according to any one of the preceding claims 1 to 9, wherein the ferroelectric layer extends in an extension plane and the polarization (P1) makes an angle with it within an angular range ([Ang]) of -20° to -160° with respect to the extension plane.

11. The method according to any one of the preceding claims 1 to 10, wherein the ferroelectric layer ($Ferro_{lay}$) is a layer of lithium niobate or of lithium tantalate.