

DESCRIPTION

TITLE OF INVENTION: METHOD FOR PREPARING A SINGLE-DOMAIN THIN LAYER MADE OF LITHIUM-CONTAINING FERROELECTRIC MATERIAL

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FIELD OF THE INVENTION

[0001] The invention relates to a structure of the piezoelectric-on-insulator
10 (POI) type. Such a structure is particularly useful in the fields of microelectronics, microsystems, photonics, etc. In particular, it can be used to form or build radio frequency (RF) components, particularly filters or resonators based on elastic wave components, such as surface elastic waves.

15 TECHNOLOGICAL BACKGROUND OF THE INVENTION

[0002] With reference to Figures 1a and 1b, which show state-of-the-art POI structures, a POI structure is typically formed by a thin piezoelectric layer 4 applied to a first face of a carrier 2. A dielectric interlayer 3 is arranged
20 between, and in contact with, the carrier 2 and the thin layer 4.

[0003] The thin layer 4 consists of a single-crystal piezoelectric material, such as lithium tantalate or lithium niobate. These materials also exhibit ferroelectric properties. Recall that a ferroelectric material is one that possesses
25 spontaneous electrical polarization in its natural state. The thin layer 4 of a POI structure must be uniformly polarized, i.e. all dipole moments must be aligned parallel to each other in a given direction.

[0004] The carrier 2 is preferably selected to be made of silicon. The substrate
30 may be a single-crystal silicon base substrate with a resistivity in excess of 1000 Ohms.cm. Alternatively, and as shown in [Fig. 1b], the carrier 2 may be formed by a base substrate 2a on which an electric charge trapping layer 2b

is arranged. In this alternative, the dielectric interlayer 3 is arranged in contact with the trapping layer 2b.

[0005] The document WO2020200986A1 proposes a method for manufacturing such a POI substrate that preserves the single-domain character of the thin layer. This document provides for transferring a layer taken from a donor substrate comprising a piezoelectric material onto the carrier 2, via a step of implanting a light species in accordance with the principles of Smart Cut™ technology. Following this transfer, the removed layer is processed in a finishing sequence comprising a heat treatment followed by a polishing step, this finishing sequence leading to the formation of the single-domain, single-crystal, piezoelectric thin layer 4. During this sequence, it was observed that the heat treatment led to the formation of a multi-domain surface portion on the sampled layer, this multi-domain surface portion then being removed by the subsequent polishing treatment, resulting in the thin layer 4 having the required single-domain quality.

[0006] However, under certain conditions, in particular when light species are implanted in high doses and/or at high currents in order to increase production rates, defects have been observed in the thin layer 4. A first type of defect observed, with reference to [Fig. 2], consists in the presence of a depression D1, or sometimes even a protuberance, on the surface of the thin layer, these depressions/protuberances D1 making the thickness of the thin layer 4 non-uniform. These defects D1, referred to as "depression-type defects" for simplicity's sake, visible on the left-hand insert of [Fig. 2], are generally circular or elliptical in shape, with dimensions (diameter or major axis) on the order of 1 micron to 100 microns, and which can sometimes have a high aspect ratio. They typically have a depth or elevation of between 1 and 30 nanometers relative to the exposed surface of the thin layer 4.

[0007] A second type of defect observed is the presence of "triangle defects" D2. These defects take the form of ferroelectric domain inversion bars with

triangular cross-sections ranging from 0.1 microns to 10 microns on a side, as can be seen in the insert on the right of [Fig. 2]. The bars emerge from the surface of the thin layer 4 and extend into the thickness of the thin layer 4 and, in some cases, through it. They are oriented in a direction antiparallel to the spontaneous polarization direction P_s of the piezoelectric thin layer 4. These triangular defects may have a density greater than $10^3/\text{cm}^2$ on the exposed surface of the thin layer 4.

[0008] Both types of defect, depressions and triangle defects, have a significant impact on the performance of devices, such as acoustic filters, formed on and in POI substrates.

OBJECT OF THE INVENTION

[0009] It is an object of the invention to address this problem at least in part. More specifically, one aim of the invention is to provide a piezoelectric-on-insulator structure whose piezoelectric thin layer is free of depression-type defects or triangular defects or, at the very least, has defects in a lower density than a piezoelectric thin layer obtained by a method of the prior art.

BRIEF DESCRIPTION OF THE INVENTION

[0010] In order to achieve this aim, the subject matter of the invention proposes a method for preparing a single-domain thin layer of lithium-containing ferroelectric material, the method comprising:

- providing a first single-domain layer of lithium-containing ferroelectric material, said layer being bonded to a carrier, the first layer having a lithium-rich surface thickness;
- finishing the first layer, this finishing comprising heat treatment of the free side of the first layer, followed by a step of thinning the first layer to form the single-domain thin layer.

[0011] The preparation method is remarkable in that it comprises, prior to the heat treatment:

- a first step of wet cleaning of the free side of the first layer, the cleaning step being able to remove the lithium-rich surface layer;
- 5 - a second step of preparing the first layer to eliminate, prevent, or limit the appearance of lithium-rich and hydrogen-rich dendrites liable to nucleate on the free side of the first layer when it is devoid of the lithium-rich surface layer.

[0012] According to other advantageous non-limiting features of the invention,
10 taken alone or according to any technically feasible combination:

- the providing of the first layer comprises:
 - implanting light species in a first face of a lithium-containing ferroelectric donor substrate to form an embrittlement plane and define the first layer between the embrittlement plane and the first face of the donor substrate;
 - 15 • assembling the first face of the donor substrate to the carrier by means of a dielectric interlayer;
 - fracturing the donor substrate at the embrittlement plane in order to transfer the first layer onto the support substrate and expose a free side of the first layer to the atmosphere, this exposure leading to the formation of the lithium-
20 rich surface thickness.
- the first cleaning step comprises brushing and dispensing deionized water onto the free side of the first layer;
- the second preparation step is a wet cleaning step of the free side of the first layer (8);
- 25 • the second preparation step comprises brushing and dispensing deionized water onto the free side of the first layer;
- the second preparation step is designed to remove dendrites and is applied at least 50 hours, preferably at least 75 hours, after the application of the first cleaning step;
- 30 • the preparation method comprises an intermediate step, between the first preparation step and the second preparation step, the intermediate step exposing the first layer to a temperature above ambient temperature;

- the second preparation step is designed to prevent or limit the appearance of dendrites and is applied less than 50 hours, preferably less than 10 hours, after the application of the first cleaning step;
- the second preparation step comprises exposing the free side of the first layer to a plasma;
- the plasma is selected from the list consisting of an O₂ plasma, an N₂ plasma and a fluorine-based plasma, such as an SF₆ or C_xH_yF_z plasma, or a combination of these plasmas;
- the support is formed by a single-piece electrically conductive or semiconductive substrate.
- the support comprises a base substrate and a trapping layer, the trapping layer being arranged between the dielectric interlayer and the base substrate;
- the first layer and the thin layer are made of a single-crystal piezoelectric material, such as lithium tantalate or lithium niobate;
- the first layer and the thin layer are made of lithium niobate;
- the dielectric interlayer comprises at least one layer of silicon oxide, silicon oxynitride, or silicon nitride.

BRIEF DESCRIPTION OF THE DRAWINGS

- [0013] 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:
- [0014] [Fig.1a]
- [0015] [Fig.1b] Figures 1a, 1b show state-of-the-art POI structures;
- [0016] [Fig.2] [Fig.2] shows the defects present in a thin layer of a POI structure;
- [0017] [Fig.3] [Fig.3] shows the steps of manufacturing a POI structure;
- [0018] [Fig. 4a]
- [0019] [Fig. 4b]
- [0020] [Fig.4c]

[0021] [Fig.4d] Figures 4a, 4b, 4c, 4d show the state of the first layer and the thin layer of a POI structure during the various stages of its manufacture;

[0022] [Fig.5] [Fig. 5] shows a method in accordance with the invention.

5 DETAILED DESCRIPTION OF THE INVENTION

[0023] We begin by recalling the steps of a method for manufacturing a POI 1 structure as presented in the introductory part of this application and shown in Figures 1a and 1b.

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[0024] This method generally provides for transferring a first ferroelectric layer 8 onto a carrier 2, the first layer 8 being taken from a single-domain ferroelectric donor substrate 5 by a transfer technique based on the implantation of light species such as hydrogen and/or helium species. In the present disclosure, the ferroelectric material of the donor substrate 5 comprises lithium. It may, for instance, be lithium tantalate or lithium niobate. In addition to ferroelectric properties, the donor substrate material also has piezoelectric properties. The ferroelectric material advantageously has a crystal direction between 30° and 60° RY. The donor substrate 5 may be a homogeneous substrate consisting entirely of ferroelectric and piezoelectric material, as shown in [Fig.3], or it may be a composite substrate consisting of a homogeneous part, e.g. made of silicon, on which a thick layer of ferroelectric and piezoelectric material lies, from which the first layer is taken.

25 [0025] In some embodiments, the carrier 2 is a single-piece conductive or semiconductive substrate. In other embodiments, the carrier 2 comprises a base substrate 2a with a surface electric charge trapping layer 2b. This trapping layer 2b is arranged on the side of the first face of the carrier 2, which is intended to receive the thin layer 4. In these embodiments shown, the dielectric interlayer 3 is in contact with the trapping layer 2b and the thin layer 4.

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[0026] According to the transfer technique based on the implantation of light species, and with reference to Figure 3b, hydrogen and/or helium are implanted into a first face 6 of the donor substrate 5 to form a buried embrittlement plane 7. The implantation dose is greater than 8×10^{16} at/cm² and/or the implantation current is greater than 20 mA, in order to achieve the conditions leading to the appearance of the defects presented in the introductory part of this application. The first layer 8 is defined in this way between the embrittlement plane 7 and the first face 6 of the donor substrate 1. Then, as shown in Figure 3c, this first face 6 of the donor substrate is joined to an exposed face 6' of the carrier 2, here via a dielectric interlayer 3. By way of example, the dielectric interlayer 3 may comprise or consist of silicon oxide, silicon oxynitride, or silicon nitride.

[0027] The donor substrate 5 is then fractured at the embrittlement plane 7, for example using moderate heat treatment and/or the application of a mechanical force. The first layer 8 is then freed from the donor substrate 5 to expose a free side 9 of the first layer 8, the other face 4 of the first layer 8 being in direct contact with the dielectric interlayer 3 of the carrier 2.

[0028] A remaining portion 5' of the donor substrate 5, after the removal of the first layer 8, can be reconditioned to remove a new layer, in a removal cycle similar to that just described.

[0029] It is generally necessary to provide for the finishing of the first transferred layer 8 bonded onto the carrier 2, to form a "useful" thin layer 4. These steps generally aim to improve the crystal quality of the first layer 8 and its surface condition (for example its roughness).

[0030] As reported in the introduction to this application, this finishing comprises a step of heat treatment of the free side 9 of the first layer 8, followed by a step of thinning the first layer 8 to form the single-domain thin layer 4.

- [0031] The step of heat treatment of the free side 9 of the first layer 8 may involve exposing this layer to a neutral or oxygen-containing atmosphere heated to a temperature of between 300°C and the Curie temperature of the ferroelectric material making up the first layer 8, and for a period of between
5 30 minutes and 10 hours. It will be noted that this step of heat treating the free side 9 of the layer 8 is separate from that which caused the donor substrate 5 to fracture. Indeed, with the layer 3 not yet having been fully released during the fracture annealing, this heat treatment cannot treat a free face thereof.
- 10 [0032] The thinning step can be carried out by mechanical/chemical polishing.
- [0033] In order to understand the origin of the defect in the thin layer 4 described in the introduction, the applicant has carried out a very precise analysis of the first layer 8 obtained at the end of the method shown in [Fig.3],
15 i.e. prior to the finishing of this first layer 8 in order to prepare the single-domain thin layer 4. These analyses were carried out on a first lithium tantalate layer 8.
- [0034] With reference to [Fig.4a], the applicant has thus observed the
20 presence of a lithium-rich surface layer 11 on the first layer 8 obtained directly after the fracturing step. This surface layer 11 consists of Li_2CO_3 . Its formation seems to be favored by the particular conditions in which this fracture step takes place. The presence of light species, hydrogen and/or helium, and the moderate temperature at which fracture occurs appear to make the lithium in
25 the first layer 8 particularly mobile and the surface of this layer 8 particularly reactive. When the remaining portion 5' of the donor substrate is removed to expose the free side 9 of the first layer 8 to the atmosphere, this surface reacts with carbon dioxide, hydrocarbons and oxygen naturally present in the atmosphere, to form the Li_2CO_3 surface layer 11. This surface thickness,
30 overlapping the first layer 8, is of the order of nanometers or more. It is stable over time, i.e. it does not change in consistency or thickness when the first layer is kept exposed to the atmosphere.

[0035] This surface layer 11 is relatively fragile, however, and the applicant has observed that it can be removed by wet-cleaning the first layer 8.

5 [0036] The applicant also observed that the first layer 8, without its lithium-rich surface layer 11, remained particularly reactive. By keeping the free side 9 of this first layer 8 exposed to the atmosphere for an extended period of time, amorphous dendrites 12, rich in lithium and hydrogen (and other species present in the atmosphere such as chlorine or fluorine) nucleate and grow on
10 the free side 9 of the first layer 8. This development is particularly noticeable after a period of between 50 and 75 hours. As illustrated in [Fig.4b], these dendrites 12 are distributed non-uniformly over the surface of the first layer 8; they accumulate densely in certain zones on the surface of layer 8, in particular on certain topologies of this surface, such as local roughness or topologies
15 caused by the emergence of dislocations, while other zones are entirely devoid of them.

[0037] The applicant has applied the finishing heat treatment step to the first layer 8 provided with these dendrite-dense zones 12 and other zones devoid
20 of these dendrites.

[0038] At the end of this heat treatment, the first layer 8 ([Fig.4c]) presented a multi-domain surface layer 13, as documented in the reference cited in the introduction to this application. The dendrites 12 had disappeared from the first
25 layer 8, probably dissolved during heat treatment. However, in areas of the first layer 8 that were initially dense with dendrites 12, the multi-domain surface layer had an atypical morphology 14, distinct from the morphology of this multi-domain surface layer 13 in areas initially devoid of dendrites. This atypical morphology 14 is characterized by a thinner multi-domain surface layer, as if
30 the presence of dendrites 12 in dense zones had limited the generation of this layer 13. Furthermore, the applicant has observed the presence of triangular defects 15 in the first layer, in a density greater than $10^4/\text{cm}^2$.

- [0039] The applicant then applied the step of thinning, by mechanical-chemical polishing, to the first layer 8 obtained after heat treatment, thus providing the thin layer 4, shown in [Fig.4d]. Note that the triangular defects 15 are made visible on the surface of the thin layer 4, after the first layer 8 has been treated by chemical-mechanical polishing to remove the multi-domain surface layer 13. However, these defects 15 were present in the first layer 8 prior to the thinning step.
- 10 [0040] The thin layer 4 obtained showed defects of the depression type 16 in the areas of atypical morphology 14 of the multi-domain surface layer 13.
- [0041] Based on these results and observations, the applicant has established a method for preparing a single-domain thin layer 4 of lithium-containing ferroelectric material. This method applies to a first single-domain layer 8 of lithium-containing ferroelectric material, bonded to a carrier 2, as shown with reference to [Fig.3] of the present application. It is shown in [Fig.5]. Under the manufacturing conditions of this layer, the first layer therefore has a lithium-rich surface thickness 11, typically Li_2CO_3 .
- 20 [0042] The preparation method is applied before finishing the first layer 8, i.e. before applying the heat treatment step to its free side 9, and before the subsequent thinning step.
- 25 [0043] This preparation method comprises a first step of wet-cleaning the free side 9 of the first layer 8. This cleaning step removes the lithium-rich surface layer, typically formed of Li_2CO_3 . It may comprise or consist of brushing the free side of the first layer while dispensing deionized water onto this free side. Experiments carried out by the applicant have shown that this cleaning process is perfectly suited to eliminating the Li_2CO_3 surface layer 11.
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[0044] The preparation method further comprise, after the first step, a second step of preparing the first layer 8. This second step aims to eliminate dendrites or prevent/limit their appearance. These amorphous, lithium-rich and hydrogen-rich dendrites 12 are liable to nucleate on the free side of the first layer 8 when it is devoid of the lithium-rich surface layer.

[0045] This second step can be implemented in several different ways.

[0046] In a first variant, the dendrites 12 are left to develop and stabilize on the surface of the first layer 8. The second preparation step then aims to remove these dendrites 12. It is therefore applied for at least 50 hours, preferably at least 75 hours, at room temperature, after the application of the first cleaning step, so that the development of dendrites 12 is effectively stabilized. Storing substrates above room temperature could reduce this minimum waiting time by 50 hours.

[0047] In one variant, therefore, the invention provides for an intermediate treatment comprising exposing the first layer 8 to a temperature higher than room temperature in order to promote dendrite development. In this way, waiting times can be reduced to under 50 hours. This may involve placing one or more substrates in an oven, for example at 50°C or in a temperature range between 27°C and 80°C. More generally, the intermediate treatment may comprise any treatment that accelerates the formation of these dendrites, such as annealing the first layer 8.

[0048] The second preparation step can be practically implemented by a step of wet-cleaning the free side, for example a cleaning step of the same type as that implemented to remove the Li_2CO_3 surface thickness 11. It may therefore comprise or consist of brushing the free side 9 of the first layer 8 while dispensing deionized water onto this free side.

[0049] In another variant, the free side of the first layer is treated to prevent the appearance of dendrites 12. This second preparation step is therefore applied less than 50 hours, preferably less than 10 hours, after the application of the first cleaning step. It may involve exposing the free side of the first layer to a plasma, for example a plasma selected from the list formed by an O₂ plasma, an N₂ plasma and a fluorine-based plasma, such as an SF₆ or C_xH_yF_z plasma, or a combination of these plasmas.

[0050] A 30-second RF plasma (at 13.55 MHz) of nitrogen (N₂), with a power of 150 W and a pressure of 50 mT, in a nitrogen flow of 75 SCCM, proved particularly effective.

[0051] Similarly, a 30-second RF plasma sequence (at 13.55 MHz), at a power of 150 W and a pressure of 50 mT, in a flow of 75 SCCM oxygen and 3SCCM SF₆ also proved effective in treating the free side 9 of the first layer 8 and preventing the appearance of dendrites 12.

[0052] The SCCM unit of measurement ("Standard Cubic Centimeters per Minute") is a physical unit of gas mass flow, in cm³/min, at a density defined by standard temperature and pressure conditions.

[0053] The claimant observed that, unexpectedly, the application of such a plasma prevented/limited the growth and appearance of dendrites 12.

	Prior art	Variant 1 (cleaning)	Variant 2 (N ₂ plasma)	Variant 2 (O ₂ /SF ₆ plasma)
Triangular defects	>1 ^{E4} -1 ^{E6} /cm ²	<1 ^{E2} /cm ²	<1 ^{E2} /cm ²	<1 ^{E2} /cm ²
Depression	1 ^{E3} -1 ^{E4} /cm ²	Not detected	Not detected	Not detected

[0054] After applying the first cleaning step and the second step to eliminate or prevent/limit the appearance of dendrites 12, the method for manufacturing

the POI structure can be continued. As already stated, this involves applying the finishing sequence to the first layer 8, in order to form the single-domain thin layer 4 of the final POI structure. This finishing sequence begins with heat treatment of the free side of the first layer, followed by thinning.

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[0055] Advantageously, particularly in the case of the first variant of the preparation method, the time between the second step of preparing the first layer and the first cleaning step is controlled to be less than 50 hours.

10 [0056] Of course, the invention is not limited to the embodiment described and variant embodiments can be added thereto without departing from the scope of the invention as defined by the claims.

Claims

1. A method for preparing a single-domain thin layer (4) of lithium-containing ferroelectric material, the method comprising:
- 5 - providing a first single-domain layer (8) of lithium-containing ferroelectric material, said layer being bonded to a carrier (2), the first layer (8) having a lithium-rich surface thickness (11);
- finishing the first layer (8), this finishing comprising heat treatment of the free side (9) of the first layer (8), followed by a step of thinning the first layer
- 10 to form the single-domain thin layer (4);
- the preparation method being characterized in that it comprises, prior to heat treatment:
- a first step of wet cleaning of the free side (9) of the first layer (8), the cleaning step being able to remove the lithium-rich surface layer;
- 15 - a second step of preparing the first layer (8) to eliminate, prevent, or limit the appearance of lithium-rich and hydrogen-rich dendrites (12) liable to nucleate on the free side (9) of the first layer (8) when it is devoid of the lithium-rich surface layer.
- 20 2. The preparation method according to the preceding claim, wherein providing the first layer (8) comprises:
- implanting light species in a first face (6) of a lithium-containing ferroelectric donor substrate (5) to form an embrittlement plane (7) and define the first layer (8) between the embrittlement plane (7) and the first face (6) of
- 25 the donor substrate (5);
- assembling the first face (6) of the donor substrate (5) to the carrier (2) by means of a dielectric interlayer (3);
- fracturing the donor substrate (5) at the embrittlement plane (7) in order to transfer the first layer (8) onto the support substrate (2) and expose a
- 30 free side (9) of the first layer (8) to the atmosphere, this exposure leading to the formation of the lithium-rich surface thickness (11).

3. The preparation method according to one of the preceding claims, wherein the first cleaning step comprises brushing and dispensing deionized water onto the free side (9) of the first layer (8).
- 5 4. The preparation method according to one of the preceding claims, wherein the second preparation step is a wet cleaning step of the free side (9) of the first layer (8).
- 10 5. The preparation method according to the preceding claim, wherein the second cleaning step comprises brushing and dispensing deionized water onto the free side (9) of the first layer (8).
- 15 6. The preparation method according to one of the preceding claims, wherein the second preparation step is designed to remove dendrites (12) and is applied at least 50 hours, preferably at least 75 hours, after the application of the first cleaning step.
- 20 7. The preparation method according to one of claims 1 to 5 comprising an intermediate step, between the first preparation step and the second preparation step, the intermediate step exposing the first layer (8) to a temperature above ambient temperature.
- 25 8. The preparation method according to one of claims 1 to 3, wherein the second preparation step is designed to prevent or limit the appearance of dendrites (12) and is applied less than 50 hours, preferably less than 10 hours, after the application of the first cleaning step.
- 30 9. The preparation method according to the preceding claim, wherein the second preparation step comprises exposing the free side (9) of the first layer to a plasma.

10. The preparation method according to the preceding claim, wherein the plasma is selected from the list formed by an O₂ plasma, an N₂ plasma and a fluorine-based plasma, such as an SF₆ or C_xH_yF_z plasma, or a combination of these plasmas.
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11. The preparation method according to one of the preceding claims, wherein the support (2) is formed by a single-piece electrically conductive or semiconductive substrate.
- 10 12. The preparation method according to one of claims 1 to 9, wherein the support (2) comprises a base substrate (2a) and a trapping layer (2b), the trapping layer (2b) being arranged between the dielectric interlayer (3) and the base substrate (2a).
- 15 13. The preparation method according to one of the preceding claims, wherein the first layer (8) and the thin layer (4) consist of a single-crystal piezoelectric material, such as lithium tantalate or lithium niobate.
14. The preparation method according to the preceding claim, wherein the
20 first layer (8) and the thin layer (4) consist of lithium niobate.
15. The preparation method according to one of the preceding claims, wherein the dielectric interlayer (3) comprises at least one layer of silicon oxide, silicon oxynitride, or silicon nitride.