

Method For Manufacturing A Crystalline Layer Of PZT Material, And Substrate For Epitaxially Growing A Crystalline Layer Of PZT Material

FIELD OF THE INVENTION

- 5 The present invention relates to a process for producing a crystalline layer of lead zirconate titanate (PZT) material and a substrate for the epitaxial growth of such a crystalline layer of PZT material.

PRIOR ART

- 10 Certain materials are not currently available as a crystalline substrate let alone as a monocrystalline substrate in the form of a large-diameter wafer. Moreover, certain materials may be available in large diameter but not with certain characteristics or specifications in terms of quality, in particular with regard to the density of defects or the required electrical or optical properties.

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SUMMARY OF THE INVENTION

- The present invention aims to overcome these limitations of the prior art by providing a process for producing a crystalline layer of PZT material, preferably a monocrystalline layer of PZT material, and a substrate for the epitaxial growth
- 20 of such a crystalline layer of PZT material, preferably of such a monocrystalline layer of PZT material. In this way it is possible to address the problem of size of the crystalline or even monocrystalline substrates of PZT material currently available.

- 25 The invention relates to a process for producing a crystalline layer of PZT material comprising the transfer of a monocrystalline seed layer of SrTiO_3 material to a carrier substrate of silicon material followed by epitaxial growth of the crystalline layer of PZT material.

- 30 In advantageous embodiments, the crystalline layer of PZT material is monocrystalline.

In advantageous embodiments, the monocrystalline seed layer has a thickness of less than 10 μm , preferably less than 2 μm , and more preferably less than 0.2 μm .

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In advantageous embodiments, the transfer of the monocrystalline seed layer of SrTiO_3 material to the carrier substrate of silicon material comprises a step of joining a monocrystalline substrate of SrTiO_3 material to the carrier substrate followed by a step of thinning of said monocrystalline substrate of SrTiO_3 material.

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In advantageous embodiments, the thinning step comprises the formation of a weakened zone delimiting a portion of the monocrystalline substrate of SrTiO_3 material intended to be transferred to the carrier substrate of silicon material.

15 In advantageous embodiments, the formation of the weakened zone is obtained by implanting atomic and/or ionic species.

In advantageous embodiments, the thinning step comprises detaching at the weakened zone so as to transfer said portion of the monocrystalline substrate of SrTiO_3 material to the carrier substrate of silicon material, in particular the
20 detaching comprises the application of thermal and/or mechanical stress.

In advantageous embodiments, the joining step is a molecular adhesion step.

25 In advantageous embodiments, the monocrystalline seed layer of SrTiO_3 material is in the form of a plurality of tiles each transferred to the carrier substrate of silicon material.

In advantageous embodiments, the carrier substrate of silicon material comprises
30 a detachable interface configured to be detached by means of a laser debonding technique and/or chemical attack and/or by means of mechanical stress.

The invention also relates to a substrate for epitaxial growth of a crystalline layer of PZT material, characterized in that it comprises a monocrystalline seed layer of SrTiO_3 material on a carrier substrate of silicon material.

- 5 In advantageous embodiments, the crystalline layer of PZT material is monocrystalline.

In advantageous embodiments, the monocrystalline seed layer of SrTiO_3 material is in the form of a plurality of tiles.

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In advantageous embodiments, the carrier substrate of silicon material comprises a detachable interface configured to be detached by means of a laser debonding technique and/or chemical attack and/or by means of mechanical stress.

- 15 The invention also relates to a process for producing a crystalline layer of material comprising PMN-PT and/or PZN-PT having a lattice parameter close to that of the PZT material comprising the transfer of a monocrystalline seed layer of SrTiO_3 material to a carrier substrate of silicon material followed by epitaxial growth of the crystalline layer of PMN-PT or PZN-PT material.

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The invention also relates to a process for producing a crystalline layer of material comprising PMN-PT and/or PZN-PT having a lattice parameter close to that of the PZT material comprising the transfer of a monocrystalline seed layer of YSZ or CeO_2 or MgO or Al_2O_3 material to a carrier substrate of silicon material followed by epitaxial growth of the crystalline layer of PMN-PT or PZN-PT material.

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The invention also relates to a substrate for epitaxial growth of a crystalline layer of material comprising PMN-PT and/or PZN-PT having a lattice parameter close to that of the PZT material, characterized in that it comprises a monocrystalline seed layer of SrTiO_3 or YSZ or CeO_2 or MgO or Al_2O_3 material on a carrier substrate of silicon, sapphire, Ni or Cu material.

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DESCRIPTION OF THE FIGURES

Other features and advantages of the invention will be better understood from reading the following detailed description with reference to the appended drawings, in which:

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- figure 1 illustrates a process for producing a crystalline layer of PZT material according to one embodiment of the invention and a substrate for the epitaxial growth of such a crystalline layer of PZT material according to this embodiment of the invention;

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- figure 2 illustrates a process for producing a crystalline layer of PZT material according to another embodiment of the invention and a substrate for the epitaxial growth of such a crystalline layer of PZT material according to this other embodiment of the invention;

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- figure 3 illustrates a process for producing a crystalline layer of PZT material according to yet another embodiment of the invention and a substrate for the epitaxial growth of such a crystalline layer of PZT material according to this other embodiment of the invention;

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- figure 4 illustrates a process for producing a crystalline layer of PZT material according to yet another embodiment of the invention and a substrate for the epitaxial growth of such a crystalline layer of PZT material according to this other embodiment of the invention;

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- figure 5 illustrates a process for producing a crystalline layer of PZT material according to yet another embodiment of the invention and a substrate for the epitaxial growth of such a crystalline layer of PZT material according to this other embodiment of the invention.

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To improve the readability of the figures, the various layers are not necessarily shown to scale.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

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Figure 1 illustrates a carrier substrate 100 of silicon material to which a monocrystalline seed layer 200 of SrTiO_3 material is transferred. Other materials for the monocrystalline seed layer 200 may be envisaged such as YSZ, CeO_2 , MgO or Al_2O_3 , these having a lattice parameter close to that of the PZT material.

10 The carrier substrate 100 of silicon material may also be replaced with a carrier substrate 100 of sapphire, Ni or Cu material. The use of silicon has the advantage of opening up the field of application of layers of PZT material not only for 300 mm-type large-scale equipment, but also making it compatible with the microelectronics industry, for which the requirements in terms of acceptance on

15 the production line for exotic material other than silicon, especially PZT, are high. The step of joining 1' the monocrystalline seed layer 200 of SrTiO_3 material to the carrier substrate 100 of silicon material is preferably carried out by way of a molecular adhesion step. This molecular adhesion step comprises a bonding step, preferably at ambient temperature, and is followed by an anneal for

20 consolidating the bonding interface which is usually carried out at high temperatures of up to 900°C or even 1100°C for a duration of a few minutes to a few hours. Regarding a carrier substrate of sapphire material, the step of joining 1' the monocrystalline seed layer to the carrier substrate is also preferably carried out by way of a molecular adhesion step using typical conditions of the same

25 order of magnitude as mentioned above. Regarding a carrier substrate of Ni or Cu material, the step of joining 1' the monocrystalline seed layer to the carrier substrate is replaced by a step of depositing the Ni or Cu material on the monocrystalline seed layer, for example via deposition by electrodeposition (ECD) or electroforming (electroplating). This technique usually includes the use

30 of a tie layer and stripping and is known per se and will not be described in more detail here.

Figure 1 schematically shows the step of joining 1' a monocrystalline substrate 20 of SrTiO_3 material to the carrier substrate 100 of silicon material. It follows a step of thinning 2' the monocrystalline substrate 20 of SrTiO_3 material after having been joined to the carrier substrate 100 of silicon material. Figure 1 schematically shows the thinning step 2', which may be implemented for example by means of chemical and/or mechanical etching (polishing, grinding, milling, etc.). Thus, the monocrystalline seed layer 200 of SrTiO_3 material may be obtained which will serve as the monocrystalline seed for a step of epitaxially growing 3' the crystalline layer 300 of PZT material on the substrate for epitaxial growth of a crystalline layer of PZT material 10 shown schematically in figure 1. Those skilled in the art would be capable of adjusting the parameters used for epitaxially growing a crystalline layer of PZT material usually used in homoepitaxy or heteroepitaxy on a bulk crystalline substrate in order to optimize the step of epitaxially growing 3' the crystalline layer 300 of PZT material on the substrate for epitaxial growth of a crystalline layer of PZT material 10 of the present invention. One possibility is that the epitaxial growth of the PZT material takes place by way of cathode sputtering, for example magnetron cathode sputtering, known to those skilled in the art. Other possibilities would be either the application of a sol-gel process including deposition at low temperature followed by various anneals at temperatures of between 350°C and 650°C or even 700°C , or epitaxial growth by way of MOCVD at typical temperatures of about 550°C using precursors known to those skilled in the art. The presence of the monocrystalline seed layer makes it possible to favorably influence the crystal quality of the crystalline layer of PZT material. In particular, it is possible to obtain a monocrystalline layer of PZT material. Incidentally, the present invention is not limited to epitaxy of the PZT material but extends to certain piezoelectric crystals of perovskite type such as PMN-PT or PZN-PT having a lattice parameter close to that of the PZT material.

It should be noted that the thermal expansion coefficient of the carrier substrate 100 dominates the thermal behavior of the substrate for epitaxial growth of a crystalline layer of PZT material 10 during the step of epitaxially growing 3' the

crystalline layer 300 of PZT material. This is due to the low thickness, preferably less than 1 μm , of the monocrystalline seed layer 200 of SrTiO_3 material relative to the total thickness of the substrate for epitaxial growth of a crystalline layer of PZT material 10, which is of the order of several tens to hundreds of μm .

- 5 Incidentally, the SrTiO_3 material is chosen so as to provide a monocrystalline seed layer having a lattice parameter that is as close as possible to the lattice parameter chosen for the crystalline layer 300 of PZT material, preferably the lattice parameter in the relaxed state in order to allow epitaxial growth resulting in as few defects as possible in the crystalline layer 300 of PZT material.
- 10 Incidentally, the material of the carrier substrate 100 advantageously has a thermal expansion coefficient which is particularly close to the thermal expansion coefficient of the PZT material for the same reasons of decreasing defects in the crystalline layer 300 obtained by epitaxy. Preferably, a carrier substrate 100 of sapphire material would therefore be used for the present invention.

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- Figure 2 schematically shows one embodiment of the process for producing a crystalline layer of PZT material which differs from the embodiment described in conjunction with figure 1 in that the monocrystalline substrate 20' of SrTiO_3 material undergoes a step of implanting 0'' atomic and/or ionic species in order
- 20 to form a weakened zone delimiting a portion 200' of the monocrystalline substrate 20' of SrTiO_3 material intended to be transferred to the carrier substrate 100' of silicon material, and in that the thinning step 2'' comprises detaching at this weakened zone so as to transfer said portion 200' of the monocrystalline substrate 20' of SrTiO_3 material to the carrier substrate 100' of silicon material, in
- 25 particular this detaching comprises the application of a thermal and/or mechanical stress. The advantage of this embodiment is thus to be able to recover the remaining part 201 of the starting monocrystalline substrate 20' of SrTiO_3 material, which may thus be used again to undergo the same process again and thus decrease costs. The substrate for epitaxial growth of a crystalline layer of
- 30 PZT material 10' thus illustrated in figure 2 is used for the step of growing 3'' the crystalline layer 300' of PZT material as already described in the process described in conjunction with figure 1. In general, the implantation step 0'' takes

place using hydrogen ions. One advantageous alternative well known to those skilled in the art consists in replacing all or some of the hydrogen ions with helium ions. A hydrogen implantation dose will typically be between $6 \times 10^{16} \text{ cm}^{-2}$ and $1 \times 10^{17} \text{ cm}^{-2}$. The implantation energy will typically be between 50 to 170 keV.

5 Thus, the detaching typically takes place at temperatures of between 300 and 600°C. Thicknesses of the monocrystalline seed layer of the order of 200 nm to 1.5 μm are thus obtained. Immediately after the detaching operation, additional technological steps are advantageously added with the aim of either strengthening the bonding interface or of restoring a good level of roughness, or
10 of correcting any defects which may have been generated in the implantation step or else to prepare the surface of the seed layer for the resumption of epitaxy. These steps are for example polishing, (wet or dry) chemical etching, annealing, chemical cleaning. They may be used alone or in a combination which those skilled in the art will be capable of adjusting.

15 Figure 3 differs from the embodiments described in conjunction with figure 1 and figure 2 in that the substrate for epitaxial growth of a crystalline layer of PZT material (10, 10') comprises a detachable interface 40' that is configured to be detached. In the case of a carrier substrate 100 of silicon material, it may be a
20 rough surface, for example of silicon material, joined with the monocrystalline seed layer during the joining step. Else, a rough interface may be present within the carrier substrate 100 of silicon material, the latter for example obtained by joining two silicon wafers. Another embodiment would be to introduce, at the face to be joined with the monocrystalline seed layer, a porous silicon layer that is
25 liable to split during the application of a mechanical and/or thermal stress, for example by inserting a blade at the edge of the wafer known to those skilled in the art or by applying an anneal. Obviously, this interface is chosen so as to withstand the other mechanical and/or thermal stresses experienced during the process of the present invention (e.g. detaching, epitaxial growth, etc.). In the
30 case of a carrier substrate of sapphire material, it may be a stack of silicon oxide, silicon nitride and silicon oxide (what is called an ONO-type structure) produced on the face of the sapphire to be joined with the monocrystalline seed layer. Such

a stack is liable to undergo detachment at the silicon nitride layer when applying a laser that passes through the sapphire carrier substrate (detaching or debonding of the "laser lift-off" type). Those skilled in the art will be capable of identifying other processes for producing this detachable interface. These various
 5 detaching configurations thus make it possible either to transfer the epitaxial layer to a final carrier which is not compatible with the growth parameters or to prepare a thick film of PZT material of freestanding type.

Figure 4 schematically shows one embodiment of the process for producing a
 10 crystalline layer of PZT material which differs from the embodiments described in conjunction with figure 1, figure 2 and figure 3 in that the monocrystalline seed layer 2000' of SrTiO₃ material is in the form of a plurality of tiles (2001', 2002', 2003') each transferred to the carrier substrate 100" of silicon material. The various tiles may take any shape (square, hexagonal, strips, etc.) and have
 15 different sizes varying from a few mm² to several cm². The spacing between the chips may also vary significantly depending on whether what is sought is a maximum density of coverage (in this case a spacing of less than 0.2 mm will preferably be chosen) or conversely a maximum spread of the tiles within the substrate (in this case the spacing may be several millimeters and even
 20 centimeters). For each tile, a person skilled in the art would be capable of applying their desired transfer and they are not limited to a particular process. Thus, it is possible to envisage applying the technical teachings described in conjunction with the process illustrated schematically in figure 1 or the technical teachings described in conjunction with the process illustrated schematically in figure 2, or
 25 even a combination of the two. Thus, it is possible to join 1'" monocrystalline substrates (2001, 2002, 2003) of SrTiO₃ material which have a size smaller than the size of the carrier substrate 100" in order to create by thinning 2'" on this latter the monocrystalline seed layers (2001', 2002', 2003') for the epitaxial growth 3'" of a crystalline layer (3001, 3002, 3003) of PZT material on each tile of the
 30 substrate for epitaxial growth of a crystalline layer of PZT material 10".

The various embodiments described in conjunction with figures 1 to 4 thus open up the possibility of co-integration of components made in the crystalline layer of PZT material with components made in the carrier substrate of silicon material. This latter may simply be a silicon substrate, but it may also be an SOI-type substrate comprising a silicon oxide layer separating a silicon substrate from a thin silicon layer. In the case of the embodiments described in conjunction with figures 1 to 4, access to the carrier substrate may be achieved simply by way of lithography and etching known to those skilled in the art. In the case of the embodiment described in conjunction with figure 4, it is also possible just to choose the locations of the tiles and their spacing.

Figure 5 schematically shows one embodiment which differs from the embodiment described in conjunction with figure 4 in that the carrier substrate 100" and subsequently the substrate for epitaxial growth of a crystalline layer of PZT material 10" comprises a detachable interface 40 that is configured to be detached, for example by means of a laser debonding (laser lift-off) technique and/or chemical attack and/or by means of mechanical stress. This would allow part of the carrier substrate 100" to be removed as already mentioned in conjunction with figure 3. One example would be the use of a carrier substrate 100 of SOI type comprising a silicon oxide layer separating a silicon substrate from a thin silicon layer. This oxide layer could be used as a detachable interface 40 by selective etching this oxide layer, for example by immersion in a hydrofluoric (HF) acid bath. This option of detaching a buried layer by means of chemical etch is particularly advantageous when it is in combination with treating a plurality of small substrates. Specifically, the range of under-etches is generally limited to a few centimeters or even a few millimeters if it is desired to retain industrially reasonable treatment conditions and times. Treating a plurality of small substrates allows the initiation of several chemical etching fronts by virtue of possible access to the buried layer between each tile, rather than just at the extreme edges of the substrates, which may be up to 300 mm in diameter. In the case of an SOI-type carrier substrate, it is thus possible to partially remove the

thin layer of silicon between the tiles in order to allow the initiation of several etching fronts.

Since the thin layer of silicon has a predetermined thickness (which may vary between 5 nm to 600 nm, or even thicker depending on the intended application), it could thus be used to form microelectronic components and thus allow the co-integration of components based on PZT materials in a single substrate.

Thus, after having formed the crystalline layer (3001, 3002, 3003) by epitaxy, it is also possible to conceive joining this structure to a final substrate and detaching, at the detachable interface 40, a part of the carrier substrate 100". The final substrate may thus provide additional functionalities which are for example incompatible with parameters of the growth carried out previously (for example final substrate of flexible plastic type or final substrate comprising metal lines).

Additionally and in general, the detachable interface is not necessarily located inside the carrier substrate but may also be located at the interface with the seed layer of SrTiO_3 material joined to this carrier substrate (for example a stack of a layer of silicon nitride between two layers of silicon oxide allows laser debonding, particularly suitable for a carrier substrate of sapphire type) as already described in conjunction with figure 3.

CLAIMS

1. A process for producing a crystalline layer (300, 300', 3001, 3002, 3003) of PZT material comprising the transfer of a monocrystalline seed layer (200, 200', 2000') of SrTiO_3 material to a carrier substrate (100, 100', 100'') of silicon material followed by epitaxial growth of the crystalline layer (300, 300', 3001, 3002, 3003) of PZT material.
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2. The process as claimed in the preceding claim, wherein the monocrystalline seed layer (200, 200', 2000') has a thickness of less than 10 μm , preferably less than 2 μm , and more preferably less than 0.2 μm .
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3. The process as claimed in one of the preceding claims, wherein the transfer of the monocrystalline seed layer (200, 200', 2000') of SrTiO_3 material to the carrier substrate (100, 100', 100'') of silicon material comprises a step of joining (1', 1'', 1''') a monocrystalline substrate (20, 20', 2001, 2002, 2003) of SrTiO_3 material to the carrier substrate (100, 100', 100'') followed a step of thinning (2', 2'', 2''') said monocrystalline substrate (20, 20', 2001, 2002, 2003) of SrTiO_3 material.
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4. The process as claimed in the preceding claim, wherein the thinning step (2'') comprises the formation of a weakened zone delimiting a portion (200') of the monocrystalline substrate (20') of SrTiO_3 material intended to be transferred to the carrier substrate (100, 100', 100'') of silicon material.
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5. The process as claimed in the preceding claim, wherein the formation of the weakened zone is obtained by implanting (0'') atomic and/or ionic species.
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6. The process as claimed in the preceding claims 4 and 5, wherein the thinning step (2'') comprises detaching at the weakened zone so as to transfer said portion (200') of the monocrystalline substrate (20') of SrTiO_3 material to the carrier substrate (100, 100', 100'') of silicon material, in particular the detaching comprises the application of a thermal and/or mechanical stress.
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7. The process as claimed in the preceding claims 3 to 6, wherein the joining step (1', 1'', 1''') is a molecular adhesion step.
- 5 8. The process as claimed in one of the preceding claims, wherein the monocrystalline seed layer (200, 200', 2000') of SrTiO_3 material is in the form of a plurality of tiles (2001', 2002', 2003') each transferred to the carrier substrate (100, 100', 100'') of silicon material.
- 10 9. The process as claimed in one of the preceding claims, wherein the carrier substrate (100, 100', 100'') of silicon material comprises a detachable interface (40, 40') configured to be detached by means of a laser debonding technique and/or chemical attack and/or by means of mechanical stress.
- 15 10. A substrate for epitaxial growth of a crystalline layer (300, 300', 3001, 3002, 3003) of PZT material characterized in that it comprises a monocrystalline seed layer (200, 200', 2000') of SrTiO_3 material on a carrier substrate (100, 100', 100'') of silicon material.
- 20 11. The substrate for epitaxial growth of a crystalline layer (300, 300', 3001, 3002, 3003) of PZT material as claimed in the preceding claim wherein the monocrystalline seed layer (200, 200', 2000') of SrTiO_3 material is present in the form of a plurality of tiles (2001', 2002', 2003').
- 25 12. The substrate for epitaxial growth of a crystalline layer (300, 300', 3001, 3002, 3003) of PZT material as claimed in one of the claims 10 or 11, wherein the carrier substrate (100, 100', 100'') of silicon material includes a detachable interface (40, 40') configured to be detached by means of a laser debonding technique and/or chemical attack and/or by means of mechanical stress.