

METHOD FOR MANUFACTURING A FILM ON A FLEXIBLE SHEET

FIELD OF THE INVENTION

5 The present invention relates to a method for manufacturing a film, notably monocrystalline, on a flexible sheet.

PRIOR ART

10 The formation of a film, notably monocrystalline, on a flexible sheet is not an easy thing.

 Indeed, the flexible sheets of interest do not in general have a seed surface suited to the growth of a film of good crystalline quality.

 Furthermore, techniques of bonding a film on a flexible sheet are also difficult to implement, because the surfaces to place in contact may not be sufficiently smooth to
15 enable direct bonding. On the other hand, the flexibility of the sheet makes good application against the film difficult.

 Furthermore, numerous adhesives would be unsuitable in view of their too high rigidity in view of the application. These adhesives may also prove to be unsuited in view of their incompatibility with the heat treatments that can be necessary for shaping the
20 monocrystalline film.

DESCRIPTION OF THE INVENTION

 One aim of the invention is thus to conceive a method for manufacturing a thin film, notably monocrystalline, on a flexible sheet, while ensuring good mechanical strength of
25 the transferred layer vis-à-vis the receiving sheet.

 To this end, the invention proposes a method for manufacturing a film, notably monocrystalline, on a flexible sheet, characterised in that it comprises the following steps:

- providing a donor substrate,
- forming an embrittlement zone in the donor substrate so as to delimit the film,
- 30 - forming the flexible sheet by deposition on the surface of the film,
- detaching the donor substrate along the embrittlement zone, so as to transfer said film onto the flexible sheet.

 “Flexible” is taken to mean in the present text a sufficiently low rigidity to allow an elastic deformation during the application of external mechanical stresses. Typically, for
35 the targeted applications, said rigidity is less than or equal to $10^6 \text{ GPa} \cdot \mu\text{m}^3$.

 Depending on the targeted applications, a certain flexibility may be sought because the targeted object is capable or has to be able to deform without deteriorating, such as for example a chip card or instead a patch that has to follow the movements of the part of

the human body on which it is applied. A certain flexibility may also be sought because the object is intended to be applied in a permanent manner on a surface with fixed but curved geometry, such as for example bottles, cylindrical recipients, windscreens, etc.

According to one embodiment, the formation of the embrittlement zone is carried out
5 by implantation of ionic species in the donor substrate.

The implanted ionic species are advantageously hydrogen and/or helium.

According to one embodiment, the detachment of the donor substrate is caused by a heat treatment.

In a particularly advantageous manner, the film is made of a material selected
10 from semiconductor materials, piezoelectric materials, magnetic materials and functional oxides.

The thickness of the film is generally comprised between 100 nm and 10 μm , preferably between 100 nm and 1 μm .

Advantageously, the flexible sheet is made of a material selected from metals,
15 glasses and ceramics.

The thickness of the flexible sheet is generally comprised between 1 and 50 μm .

The deposition of the flexible sheet may be implemented by one of the following techniques: physical vapour deposition, chemical vapour deposition, electrochemical deposition, spin coating, lacquering and spraying.

20 Preferably, the flexible sheet has a rigidity R comprised between 100 $\text{GPa}\cdot\mu\text{m}^3$ and $10^6 \text{GPa}\cdot\mu\text{m}^3$, said rigidity being defined by the formula:

$$R = \frac{E \times H^3}{12 \times (1 - \nu^2)}$$

where E is the Young's modulus of the material of the sheet, H the thickness of said sheet and ν the Poisson coefficient.

The method may comprise, before the formation of the flexible sheet, the formation
25 of an intermediate layer by deposition on the surface of the film.

According to one embodiment, said intermediate layer may be configured to increase the adherence of the flexible sheet vis-à-vis the film.

Optionally, said intermediate layer may form an electrical contact with the film.

Furthermore, the method may comprise, after the detachment of the donor
30 substrate, the deposition of an additional film on the face of the transferred film opposite to the support.

Advantageously, the residue of the donor substrate at the end of the detachment is recycled with a view to the implementation of a new film.

In the case where the donor substrate has a non-flat surface obtained before the
35 formation of the embrittlement zone, before the recycling, the residue of the donor

substrate is subjected to an operation of regeneration of its surface involving a removal of material that is substantially zero or conforming to the topology of said residue.

According to one embodiment, the donor substrate comprises a plurality of pads laid out on the surface of a wafer, each pad comprising an embrittlement zone delimiting a
5 respective film to transfer, and the flexible sheet is deposited on the surface of said pads.

DESCRIPTION OF THE FIGURES

Other characteristics and advantages of the invention will become clear from the detailed description that follows, with reference to the appended drawings, in which:

- 10 - figure 1A is a schematic sectional view of a donor substrate;
- figure 1B illustrates in a schematic manner the formation of an embrittlement zone in the donor substrate of figure 1A;
- figure 1C illustrates in a schematic manner the deposition of the flexible receiving sheet on the donor substrate of figure 1B;
- 15 - figure 1D illustrates in a schematic manner the structure resulting from the detachment of the donor substrate along the embrittlement zone;
- figure 1E illustrates the deposition of an additional film on the transferred film at the end of the detachment;
- figure 2A illustrates in a schematic manner the formation of an embrittlement zone
20 in the donor substrate;
- figure 2B illustrates in a schematic manner the deposition of an intermediate layer on the donor substrate of figure 2A;
- figure 2C illustrates in a schematic manner the deposition of the flexible receiving sheet on the intermediate layer of figure 2B;
- 25 - figure 2D illustrates in a schematic manner the structure resulting from the detachment of the donor substrate along the embrittlement zone;
- figure 3A illustrates in a schematic manner a donor substrate having a curved surface;
- figure 3B illustrates the formation of an oxide layer on the surface of the donor
30 substrate of figure 3A;
- figure 3C illustrates the formation of an embrittlement zone in the substrate of figure 3B;
- figure 3D illustrates in a schematic manner the deposition of the flexible sheet on the donor substrate of figure 3C;
- 35 - figure 3E illustrates in a schematic manner the structure resulting from the detachment of the donor substrate along the embrittlement zone;

- figures 4A-4D illustrate in a schematic manner the steps of a method according to another embodiment of the invention, involving the formation of a non-flat topology of the surface of the film to transfer;

5 - figures 5A-5C illustrate in a schematic manner the steps of a method according to another embodiment of the invention.

For reasons of legibility of the figures, the different elements are not necessarily represented to scale. Reference signs present from one figure to the next represent the same elements.

10 **DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION**

Generally speaking, the invention provides for the formation of the flexible sheet by deposition on a donor substrate that has been embrittled beforehand so as to delimit a thin film. Said thin film is next transferred onto the flexible sheet by detachment of the donor substrate. The sheet may be constituted of a single material or a stack of at least
15 two different materials, deposited successively on the donor substrate.

Figure 1A illustrates a donor substrate 10 which comprises at least one superficial portion constituted of the material intended to form the thin film. Although said donor substrate is represented in the form of a bulk substrate, it could also be formed of a stack of layers of different materials, of which a superficial layer constituted of the material
20 intended to form the thin film. In particular, the thin film may correspond to a layer of this stack produced by epitaxy.

Advantageously, the material intended to form the thin film is selected from: semiconductor materials (for example: silicon, silicon carbide, germanium, III-V compounds such as AsGa, InP, GaN, II-IV compounds such as CdTe, ZnO), piezoelectric
25 materials (for example: LiNbO₃, LiTaO₃, PZT, PMN-PT), magnetic materials and functional oxides (for example: ZrO₂, YSZ: yttrium stabilised ZrO₂, SrTiO₃, GaO₂). These examples are not limiting.

Preferably, the material intended to form the thin film is monocrystalline. It may also be polycrystalline, and in this case emphasis is often placed on optimising its conditions of
30 formation in order to obtain for example a particular density and a size of crystalline grains and/or a preferential crystalline orientation, and/or an optimised roughness.

With reference to figure 1B, an embrittlement zone 11, which delimits a superficial film 12 intended to be transferred, is formed in the donor substrate 10.

The thickness of the transferred film is defined by the depth of the embrittlement
35 zone 11 in the donor substrate 10. Advantageously, this depth is comprised between 100 nm and 10 μ m, preferentially between 100 nm and 1 μ m.

The formation of the embrittlement zone 12 in the donor substrate 10 may be carried out by implantation of ionic species (shown schematically by the arrows in figure 1B).

Advantageously, the implanted species are hydrogen ions and/or helium ions. The implantation energy makes it possible to define the depth of the implantation zone 11. The implantation dose is chosen in order to enable the detachment of the film 12 after the application of a suitable treatment. The implantation dose is chosen sufficiently low so as not to induce the formation of bubbles as of the implantation step. The ionic species, the energy and the implantation dose are chosen as a function of the material of the donor substrate 10. These conditions have been the subject of numerous publications and are known to those skilled in the art.

With reference to figure 1C, a flexible sheet 20 is formed on the surface of the film 12 which, at this stage, still forms part of the donor substrate 10.

In contrast to bonding techniques, the flexible sheet does not pre-exist and is formed directly on the donor substrate. The following deposition techniques may be implemented for the formation of said film: physical vapour deposition (PVD), chemical vapour deposition (CVD), deposition by electrodeposition or electroforming (electroplating or electrochemical deposition (ECD)), spin coating, lacquering and spraying. These techniques are known *per se* and will not be described in greater detail here, those skilled in the art being capable of selecting the most suitable technique as a function of the material of the flexible sheet. Deposition techniques at relatively low temperature are preferred, in order not to initiate a premature detachment of the donor substrate.

The flexible sheet is advantageously made of a material selected from metals (for example: Ni, Cu, Cr, Ag, Fe, Co, Zn, Al, Mo, W and alloys thereof), glasses and ceramics (for example: silica (SiO₂), alumina (Al₂O₃), polycrystalline AlN, polycrystalline silicon, polycrystalline SiC). These examples are not limiting.

The thickness of the flexible sheet is typically comprised between 1 and 50 µm.

The rigidity of the sheet has to be sufficiently low to ensure the flexibility of said sheet with regard to the targeted application, but sufficiently high to enable in a first instance the transfer of the film 12 onto the sheet 20, and to do so without formation of blisters.

The rigidity R may be estimated by the formula:

$$R = \frac{E \times H^3}{12 \times (1 - \nu^2)}$$

where E is the Young's modulus of the material of the sheet, H the thickness of said sheet and ν the Poisson coefficient.

Sufficiently low rigidity to ensure flexibility is taken to mean a rigidity less than or equal to 10⁶ GPa.µm³. As an indication, it will be noted that the rigidity of a layer of 43 µm of silicon is around 10⁶ GPa.µm³, whereas the rigidity of a layer of 92 µm of silicon is around 10⁷ GPa.µm³.

Sufficiently high rigidity to avoid the formation of blisters during the transfer is taken to mean a rigidity greater than or equal to $100 \text{ GPa} \cdot \mu\text{m}^3$.

Furthermore, care is taken to ensure that the adherence of the sheet on the donor substrate is sufficient to avoid the detachment of the sheet during the film transfer method.

5 This adherence may be improved by the deposition of an adhesion layer on the donor substrate before the deposition of the sheet. For example, said adhesion layer may be made of one of the following materials: Ti, Cr, Pt, Ta, TiW, Si_3N_4 , TiN, CrCu.

More generally, at least one intermediate layer may be deposited on the film 12 before the deposition of the flexible sheet. It may also be in particular a stack of layers.
10 Apart from a potential adhesion function, such an intermediate layer or stack may notably have the function of avoiding the diffusion of chemical species to the film 12 during the deposition of the sheet 20, and/or to form an electrical contact on the film 12, and/or to form an optical index jump, and/or to form a reflective layer such as a Bragg mirror and/or instead minimise a discontinuity in acoustic impedance. Naturally, those skilled in the art
15 are capable of choosing the suitable materials and their thickness according to the mechanical, electrical, optical, thermal, acoustic or chemical function of the intermediate layer or stack.

The thickness of the intermediate layer(s) remains sufficiently low so that the rigidity of this layer or stack does not penalise the flexibility of the sheet.

20 When an important difference exists between the thermal expansion coefficients of the sheet and the film (typically a difference greater than $5 \times 10^{-6} \text{ K}^{-1}$), the material of the sheet is chosen to demonstrate sufficient ductility in order that the transferred film does not suffer damage (for example of fissure type) during the transfer method. Sufficient ductility is taken to mean that the elastic limit of the sheet is less than the product of the
25 elastic limit of the film and the thickness ratio between the sheet and the film.

With reference to figure 1D, the donor substrate 10 is next detached along the embrittlement zone 11, so as to transfer said film 12 onto the flexible sheet 20. At the end of this detachment a residue 10' of the donor substrate remains, which may potentially be recycled with a view to another use.

30 The detachment is caused by a treatment of the stack of the sheet 20 on the donor substrate 10. Said treatment may be for example thermal, mechanical or a combination of these two types of treatment. This type of treatment is well known notably within the context of the Smart Cut™ method and thus will not be described in detail here. In the case of a heat treatment, the thermal budget of this treatment is generally greater than the
35 thermal budget of deposition of the flexible sheet.

The film 12 may potentially serve as a seed for the deposition of an additional film 13 (cf. figure 1E).

The structure formed of the flexible sheet 20 and the film 12 (and a potential additional film) may be used to form devices which notably have applications in microelectronics, photonics or optics. Such a structure may also enter into the manufacture of sensors or transducers, or membranes for fuel cells.

- 5 Below are described several examples (non-limiting) of application of the method according to the invention.

Example 1: formation of a lithium niobate film on a copper sheet

- 10 Lithium niobate is a piezoelectric and pyroelectric material remarkable in that it conserves its piezoelectric properties up to high temperatures. Its Curie temperature is around 1140°C, whereas numerous other materials lose their properties as of temperature ranges of the order of 100 to 250°C. It thus represents an interesting material for systems exploiting piezoelectricity and/or pyroelectricity in these temperature ranges.

- 15 For example, they may be systems for recovering energy by recovery of the energy of vibrations and other deformations of a mechanical system operating in a hostile environment in temperature ranges above 250°C. They may also be piezo or pyroelectric sensors dedicated to the measurement of mechanical deformation, temperature or to the exchange of data by emission/reception of radiofrequency waves.

- 20 To do so the lithium niobate film has to be able to deform sufficiently easily. This material is monocrystalline and of good quality when it is produced by drawing out of ingots then cut into bulk wafers of several hundreds of μm thickness. In thin films, when it is produced by deposition it is in general polycrystalline, at best quasi-monocrystalline but very defective. Having available thin films of lithium niobate of good quality on a flexible sheet makes it possible to address application fields such as portable or wearable sensors (integrated in textiles for example), and the "Internet of Things" (IoT). These examples
25 are not limiting.

Helium ions are implanted in a lithium niobate substrate 10 so as to form an embrittlement zone 11 and delimit a thin LiNbO_3 film 12 (cf. figure 2A). The thickness of the film 12 is of the order of 1 μm .

- 30 An adhesion layer 21 constituted of a Cr/Cu alloy is deposited on the film 12 by a PVD technique (cf. figure 2B). A copper sheet 20 is next deposited on said adhesion layer, by an electrochemical deposition technique (cf. figure 2C). The thickness of said sheet is of the order of 20 μm .

- 35 Next, an annealing is applied at a temperature of 300°C, in order to cause the detachment of the donor substrate 10 along the embrittlement zone 11 (cf. figure 2D).

Example 2: formation of a yttrium stabilised zirconia film on a sheet of nickel

Yttrium stabilised zirconia is generally in the form of polycrystalline ceramic, and more rarely in the form of monocrystalline substrate.

One use of this material is based on its ion conduction properties. It then serves as
5 solid membrane to play the role of electrolyte in SOFC (Solid Oxide Fuel Cell) systems. Such systems, when they have to be miniaturised (this is then known as micro-SOFC) have interest to evolve on the one hand to thin membranes, typically below several μm thickness, and on the other hand monocrystalline. Such systems operate at high temperature (typically 550-700°C) and are subjected to strong thermomechanical loads. In
10 order to make the membrane more resistant, it will advantageously be given the possibility of deforming slightly.

A monocrystalline YSZ substrate 10 is supplied.

Hydrogen ions are implanted in said substrate 10 so as to form an embrittlement zone 11 and delimit a thin YSZ film 12 (cf. figure 2A). The thickness of the film 12 is of the
15 order of 1 μm .

An adhesion layer 21 constituted of a Cr/Cu alloy is deposited on the film 12 by a PVD technique (cf. figure 2B). A nickel sheet 20 is next deposited on said adhesion layer by an electrochemical deposition technique (cf. figure 2C). The thickness of said sheet is of the order of 20 μm .

20 Next, an annealing is applied at a temperature of 300°C, in order to cause the detachment of the donor substrate 10 along the embrittlement zone 11 (cf. figure 2D).

Example 3: formation of a monocrystalline silicon film on a curved glass sheet

In the field of the production of screens or other optical parts (lenses, mirrors, etc.),
25 the production of non-flat or curved parts makes the use of thin films of monocrystalline materials such as silicon difficult. This example aims to make available a thin silicon film on a glass sheet having a certain curvature. This silicon film could for example serve to produce high performance transistors, for example for the purposes of producing high definition ultra-compact and curved screens.

30 A bulk monocrystalline silicon substrate 10 is supplied.

The curved shape that it is wished to follow is produced by etching in this silicon substrate. In the case of figure 3A, the shape chosen is concave with a more pronounced rise on the edges. Any other profile – parabolic, elliptic, corrugated, etc. - will be possible. This shape could be produced thanks to an etching by mechanical machining. Those
35 skilled in the art will know how to adapt the etching technique the most suited to the desired shape and dimension.

The substrate 10 is subjected to a thermal oxidation to produce a SiO_2 layer 14 of 0.2 μm thickness (cf. figure 3B). Hydrogen ions are next implanted in said substrate 10 so

as to form an embrittlement zone 11 and delimit a thin film 12 of monocrystalline silicon (cf. figure 3C). The thickness of the film 12 is of the order of 0.5 μm .

A sheet 20 made of silica, in other words made of glass, is deposited on the film 12 by a deposition technique at low temperature, typically below 200°C so as not to cause an untimely detachment along the embrittlement zone (cf. figure 3D). The thickness of said sheet is of the order of 20 μm . Those skilled in the art will know how to choose in these conditions the deposition technique the most suited notably in terms of temperature and desired final thickness.

Next, an annealing is applied at a temperature of 500°C, in order to cause the detachment of the donor substrate 10 along the embrittlement zone 11 (cf. figure 3E).

Example 4

Example 4 targets acoustic wave structures such as radiofrequency (RF) filters for example. In certain structures it is sought to avoid reflections of parasitic waves on the rear face of the substrates and or layers considered. One means consists in making geometrically imperfect the interfaces and rear surfaces, notably by introducing voluntary texturing or other types of roughness. This constraint is difficult or even impossible to satisfy if the use of certain thin films of monocrystalline materials such as LiTaO_3 for example is envisaged, and this is so without resorting to the introduction of complex stacks of additional intermediate layers. Example 4 targets such an object.

A bulk monocrystalline LiTaO_3 substrate 10 is supplied.

Hydrogen ions are implanted in said substrate 10 through the surface 10a so as to form an embrittlement zone 11 and delimit a thin film 12 of monocrystalline LiTaO_3 (cf. figure 4A). The thickness of the film 12 is of the order of 1.5 μm .

A texturing of the surface 10a is created by photolithoetching (cf. figure 4B). In this example the implantation takes place before the texturing step but it could take place after.

Those skilled in the art will know how to adapt the technique the most suited to the shape and dimensions desired for the texture. It is possible for example to choose a nanoimprint lithography technique to define patterns of characteristic slightly submicronic lateral dimensions, over a depth of the order of 0.05 μm . In an alternative, the texturing is obtained by roughening by cathodic sputtering effect. According to another alternative, preferably implemented before the implantation step, the texturing may be obtained by a sanding of the surface of the substrate 10.

A sheet 20 made of silica is deposited on the film 12 by a low temperature deposition technique, typically below 100°C so as not to cause an untimely detachment along the embrittlement zone (cf. figure 4C). The thickness of said sheet is of the order of 10 μm . Those skilled in the art will know how to choose in these conditions the deposition

technique the most suited notably in terms of temperature and desired final thickness. As an alternative, the sheet 20 may be made of metal instead of being made of silica.

Next, an annealing is applied at a temperature of the order of 200°C, in order to cause the detachment of the donor substrate 10 along the embrittlement zone 11 (cf. figure 4D).

Example 5: Case of a donor substrate comprising a plurality of pads

According to one embodiment of the invention, the non-flat topology of the donor substrate results from the formation of a plurality of pads 1001 laid out on the surface of a wafer 1000 (cf. figure 5A).

The pads are advantageously formed of a material selected from semiconductor materials, piezoelectric materials, magnetic materials and functional oxides. The pads are advantageously monocrystalline. Each pad may be put in place on the wafer by bonding, individually or collectively.

The pads may have any appropriate size and shape as a function of the targeted application. The pads may be laid out in a regular manner on the wafer, for example to form a sort of grid pattern.

The main surface of each pad 1001 is parallel to the main surface of the wafer 1000. However, in so far as the thickness of each pad is not controlled with sufficient precision, there may exist a slight difference in thickness from one pad to the next (for example of the order of 1 or 2 μm thickness). As a result, the surface constituted of all of the surfaces of the pads has differences in levels, typically in the form of steps (the amplitude of these variations has been voluntarily exaggerated in figure 5A). These different steps thus form a non-flat topology of the surface of the wafer.

In general, as described for example in the documents FR 3 041 364 and US 6,562,127, the pads are intended for the transfer of a superficial monocrystalline film onto a final support. To this end, an embrittlement zone 1011 is formed in each pad, before or after its putting in place on the wafer, to delimit a respective film 1012 to transfer, for example by an implantation as described above.

Unlike the methods described in the aforementioned documents, which involve bonding of the main face of each pad on the final support, the invention proposes depositing the flexible sheet 20 on all of the pads laid out on the surface of the wafer (cf. figure 5B). One is thus free of problems of assembly linked to the difference in height of the different pads.

Next, each pad is detached along the respective embrittlement zone 1011, so as to transfer the corresponding film 1012 onto the flexible sheet 20 (cf. figure 5C).

Advantageously, the transferred films are more rigid than the flexible sheet. Consequently, if the use of the composite structure thereby obtained involves deforming it

in a permanent or dynamic manner, the sheet constitutes a flexible junction between the pads, which absorbs the stresses due to these deformations instead of transmitting them to the pads.

5 Whatever the embodiment considered, at the end of the detachment of the donor substrate a residue 10' remains.

 If a recycling of said donor substrate is envisaged, it is possible to implement reconditioning operations, notably with the aim of regenerating the surface of the donor substrate which could have been damaged during the detachment. These operations may
10 notably comprise steps of cleaning, etching, annealing, smoothing and planarization, for example by polishing.

 In the case where the donor substrate has a particular topology (curvature, roughness, texturing, etc.) that has been produced before the embrittlement step, the residue of the donor substrate has a topology identical to the initial topology of the donor
15 substrate. It may appear advantageous for questions of cost to conserve this topology that had been initially created in the donor substrate, with a view to avoiding reforming it systematically after each recycling. In this case planarization methods are avoided, while favouring methods for removing material conformal in thickness, or even with substantially zero removal of material (that is to say below 30 nm), such as for example plasma
20 etchings or smoothing annealings.