METHOD FOR RECYCLING A SOURCE SUBSTRATE

GENERAL TECHNICAL FIELD

The field of the invention is that of semiconductor substrates used in the electronics, optics or optoelectronics industry.

The invention more precisely relates to the recycling of semiconductor substrates from which a thin layer of material has been removed.

PRIOR ART

SOI (silicon-on-insulator) structures are structures consisting of a multilayer comprising a very thin layer of silicon on an insulator layer, itself generally on a substrate. These structures are increasingly used in the electronics industry because of their superior performance.

This type of structure is generally produced using Smart-Cut™ technology and Figures 1a-c show the main steps for producing an SOI wafer.

Figure 1a shows a source or "donor" substrate 1 one side of which is subjected to implantation via bombardment with ionic species 10 (for example H^+ ions) so as to create, at a certain depth in the substrate, a weakened interface 2. As illustrated in Figure 1b, the side of the source substrate 1 which was subjected to the implantation is brought into intimate contact with a support or "receiver" substrate 3 so as to produce a bond via molecular adhesion. This support substrate 3 may have an insulating layer on its surface, this insulating layer being obtained for example by oxidation of the surface. Next, as shown in Figure 1c, the source substrate is cleaved along a median plane of the weakened interface 2 so as to transfer to the support substrate 3 the part of the source substrate 1 located between its external side and the weakened interface 2, the transferred part forming a layer 4.

As illustrated in Figure 1c, an "exclusion zone" which corresponds to a non-transferred part of the thin layer 4 is formed on the periphery of the support substrate 1.

This is because, as illustrated very schematically in Figure 1b, the source substrate 1 and the support substrate 3 respectively comprise on their peripheries a bevel or "edge rounding" 1a and 3a the role of which is to make handling the substrates easier and to prevent edge flaking which could occur if these edges were sharp, such flakes being a source of particulate contamination of the wafer surfaces.

However, the presence of such a bevel prevents good contact between the support substrate 3 and the source substrate 1 at their periphery. The bonding force obtained at the periphery of the assembly is therefore insufficient to retain, over its entire diameter, the part of the source substrate 1 to be transferred to the support substrate 3. The layer 4 to be transferred has a small thickness, limited to several hundred nanometres, because it is formed by implantation. This small thickness weakens it and it breaks at the bevel during detachment. The detached layer 4 of the source substrate 1 is therefore not transferred at the periphery of the support and there is therefore a residual part that creates a zone 5 that is in relief relative to the detachment surface, this peripheral zone 5 taking the form of a "ring".

It is necessary to remove this ring if it is desired to recycle the source substrate 1 stripped of the layer 4, this being called the "negative", in order to reuse it as a "positive" in order to transfer a new thin layer. Furthermore, zones of material are sometimes not transferred and may remain on the surface of the negative. The expression "regions in relief" will be understood in the remainder of the description of the invention to mean all of the zones 5 in relief relative to the detachment surface in general, the

invention in no way being limited to removal of the ring alone, even if it represents most of the regions in relief, but also relating to removal of non-transferred zones present on the surface of the negative.

Techniques have been provided to remove the regions 5 in relief and allow the source substrate 1 to be recycled. Document EP 1 427 002 in particular proposes a chemical-mechanical polishing of the surface of the source substrate 1, and use of a water, air or fluid jet, a laser beam, shock waves or ion bombardment locally targeted at the regions 5 in relief, in particular targeted at the interface 2.

However, none of these methods are completely satisfactory. The materials of certain source substrates (SiC, GaN, AlN, AlGaN, etc.) are hard and difficult to polish. The chemical-mechanical polishing is therefore long and costly. Energy-based techniques, such as the use of a laser beam, are not selective and may damage the rest of the source substrate unless they are controlled very precisely.

In addition, substrates have increasingly large diameters (six inches for example), thereby amplifying the aforementioned difficulties. In particular there is a risk that defects, for example micro-scratches, will form.

SUMMARY OF THE INVENTION

The present invention aims to make removal of the ring of residual material on a donor substrate easier, and therefore to make recycling this substrate easier, by reducing the duration, the quality and the cost of the recycling operations.

For this purpose, the present invention relates to, according to a first aspect, a process for recycling a source substrate comprising a surface region and regions in relief on the surface region,

said regions in relief corresponding to residual regions of a layer of the source substrate, said residual regions not being separated from the rest of the source substrate during a prior removal step implementing a separation at a weakened interface formed by damaged material of the source substrate, the surface region corresponding to part of the weakened interface not separated from the rest of the source substrate during the prior removal step, characterized in that it comprises selective electromagnetic irradiation of the source substrate at a wavelength such that the damaged material of the surface region absorbs the electromagnetic irradiation.

It is thus possible to carry out electromagnetic irradiation at a defined wavelength over the entire area of the source substrate to be recycled, only the damaged material located at the base of the ring or the non-transferred regions in relief will absorb the radiation and then will be selectively removed. The power of the radiation is thus chosen so that the heating of the material to be removed does not damage neighbouring zones, resulting in the substrate being in an optimal state at the end of the recycling operation.

According to other advantageous and non-limiting features:

- the regions in relief correspond to a ring of material from the layer of the source substrate and/or to non-transferred zones of material from the layer of the source substrate distributed randomly on the surface region;
- the selective electromagnetic irradiation is carried out over the entire area of the source substrate;
- the selective electromagnetic irradiation is controlled by an optical device that detects the regions in relief so that the irradiation is carried out locally on the regions in relief;

- said optical device detects the regions in relief via the difference in optical contrast between the damaged material of the weakened interface and the undamaged material of the source substrate;
- the source substrate consists of a bulk material chosen from at least one of the following materials: SiC or a binary, ternary or quaternary III-N material; or consists of a composite structure of the GaNOS, InGaNOS, SiCOI or SiCopSiC type;
- the weakened interface is generated by implanting ionic species into the source substrate;
- the process comprises implementation of a chemical-mechanical polishing of the surface region of the source substrate following the selective electromagnetic irradiation;
- said chemical-mechanical polishing uses a colloidal acid solution enriched with an additive, in particular diamond particles and/or an oxidizing agent;
- the selective electromagnetic irradiation of the source substrate is carried out by means of a laser;
- the material of the source substrate is GaN and the laser emits at a wavelength longer than or equal to 370 nm;
- the material of the source substrate is SiC and the laser emits at a wavelength longer than or equal to 415 nm;
- the laser is a pulsed-mode yttrium-aluminium-garnet laser;
- the laser has a power density of 0.1 to 2 J/cm^2;
- the process comprises epitaxial growth of at least one layer of material on one surface of the source substrate; and
- said epitaxial growth of material is carried out on the surface exposed following the selective electromagnetic irradiation.

According to a second aspect, the invention relates to a source substrate recycled by a process

according the first aspect of the invention so as to be reused.

The invention lastly relates, according to a third aspect, to a process for transferring a layer from a source substrate, recycled according to the second aspect of the invention, to a support substrate comprising steps of:

- generating a weakened interface in the recycled source substrate at a depth bounding the thickness of the layer;
- bringing the recycled source substrate and a support substrate into contact; and
- fracturing heat treatment.

SUMMARY OF THE FIGURES

Other features and advantages of the present invention will become clear on reading the description which follows of a preferred embodiment. This description will be given with reference to the appended drawings in which:

- Figures 1a-c, described above, are diagrams illustrating the mains steps of the Smart-Cut™ process and explaining how a ring forms;
- Figure 2 is a diagram showing the steps of an embodiment of a recycling process according to the invention associated with a transferring process; and
- Figure 3 is a diagram showing a residual region in detail.

DETAILED DESCRIPTION

The invention is based on the fact that weakening the material of a source substrate 1 damages its crystal structure to the extent that its optical transmission spectrum is singularly modified. The bands of the spectrum in which the material is transparent to, or on the contrary absorbs, radiation are

effectively moved because of the damage to the crystal structure. The invention provides, in a general way, for use of electromagnetic irradiation of the substrate to be recycled at a wavelength at which the damaged material absorbs while the material, the crystal structure of which is not damaged, or only slightly damaged, does not absorb or absorbs much less.

As explained above, and as shown in Figure 2, the process 200 for recycling a source substrate 1 according to the invention follows a prior process 100 for separating a layer 4 from a source substrate 1, this process 100 advantageously comprising the transfer of a layer 4 from the source substrate 1 to a support substrate 3.

The invention is however not limited to such a transfer, but targets more generally any separation of a layer 4 following the weakening of the source substrate 1, especially by implantation of ionic species. Moreover, since the support substrate 3 acts to provide the layer 4 with stiffness, the substrate may not only be bonded to the layer 4 before separation but may also be deposited onto the layer 4 by any deposition method, typically epitaxial growth. Furthermore, the layer 4 may be thick and rigid enough to be self-supporting (it is possible to handle it without it rolling up or without it breaking) or at least it may be used without an external source of rigidity being needed. Thus, in the absence of a supporting substrate 3, separation or detachment of the layer 4 is spoken of, and not transfer.

Following this prior process 100, the negative, i.e. the source substrate 1 stripped of the transferred layer 4, comprises regions 5 in relief relative to a surface region 6, these regions 5 in relief being residual regions of the layer 4, and therefore consist of left-over material from the layer 4.

It will be noted that a "surface region" is spoken of and not only a surface. This point will be clarified hereinbelow.

Advantageously, the source substrate 1 consists of a material chosen from at least one of the following materials: SiC or a binary, ternary or quaternary III-N material such as GaN, AlN, AlGaN or InGaN. The source substrate 1 may also consist of a composite structure comprising a mechanical support to which a layer of material from the above list has been bonded. Typically the composite structure may be SiCopSiC (a layer of SiC bonded to a polycrystalline SiC substrate), or GaNOS (a layer of GaN bonded to a sapphire substrate). The source substrate 1 may also be a composite structure on which a layer has been deposited, this is the case for InGaNOS in which a layer of InGaN is deposited by epitaxy on a GaNOS structure. The support substrate 3 consists of a material chosen from at least one of the following materials: AlN, GaN, SiC, sapphire, a ceramic and/or a metal alloy. The invention is however not limited to any particular combination of material.

Steps of the transfer and recycling processes

The prior separating process 100 advantageously consists, in the case of a transferring process, in separation of the source substrate 1 at a weakened interface 2 formed of a damaged material separating the layer 4 from the rest of the source substrate 1.

In this case, the transferring process 100 comprises, in an implementation that is particularly advantageous, three steps. First the interface 2 is created by a step 110 of weakening the material. Advantageously, this step consists in implantation of ionic species. The surface of the substrate 1 is bombarded by a beam of ionic species with a defined energy and dose. These ionic species penetrate into the

material to a preset depth which defines the thickness of the layer 4.

Once the weakened interface 2 has been generated, the source substrate 1 and the support substrate 3 are brought into contact during a second step 120 so as to bond by molecular adhesion. Prior to this step, the source substrate 1 and/or the support substrate 3 may optionally be oxidized. Depending on the nature of the material, and especially in the case of III-N materials, sapphire and SiC, a layer of silicon dioxide (SiO_2) or of silicon nitride (Si_xN_y) may be deposited, this layer increasing the bonding energy between the surfaces which have been brought into contact.

A fracturing heat treatment 130 completes the transfer process. A temperature increase strengthens the bond between the two substrates 1 and 3 and also causes a fracture in the implanted region (weakened interface 2). The layer 4 is detached from the substrate 1, except at the periphery and on other regions randomly distributed over the surface of the substrate, these all forming regions 5 in relief.

It is important to note that the weakened interface 2 is in fact a region with a volume, as may be seen in the schematic representation of Figure 3. The weakened interface 2 in fact has a thickness that corresponds to the deepest and shallowest penetration of the ionic species during the bombardment. This is because, although implanted into the source substrate 1 with a high precision, the ionic species are in fact distributed over a narrow band with a peak at its median plane, roughly with a Gaussian distribution, meaning that the weakened interface 2 is a volume of damaged material and not a plane, the damage being greatest in the median plane.

The fracture plane along which the layer 4 is detached from the substrate 1 is therefore located at this median plane, in the thickness of the weakened interface 2: part of the weakened interface 2 is

therefore found on each of the surfaces of the layer 4 and of the substrate 1.

Thus, the surface region 6 indicates that part of the weakened interface 2 that is not separated from the rest of the source substrate 1, this part consisting of a layer of damaged material of variable thickness located over the entire area of the source substrate 1, as may be seen in Figure 3.

Thus, since they are still attached to the negative of the substrate 1, the regions 5 in relief have at their base the whole thickness of the weakened interface 2.

Absorption of the electromagnetic radiation by the damaged material that forms the remnants of the weakened interface 2 makes it possible to remove the surface region 6, and therefore to detach the residual region 5 from the source substrate 1.

Implantation of ionic species into a material effectively damages the crystal structure of the material by creating various defects, until the material becomes amorphous, therby modifying the optical absorption spectrum of the material. The recycling process 200 according to the invention also comprises at least one substep 210 of electromagnetic irradiation of the source substrate 1.

By carrying out selective electromagnetic irradiation at a defined wavelength, only the damaged material of the interface 2 will absorb the energy of the radiation and be selectively transformed, the transformation advantageously being destruction due to substantial heating. The rest of the material is transparent to the radiation and will quite simply be passed through without modification. As explained above, the residual parts of the interface 2 form the surface region 6 and are located in particular interposed between the regions 5 in relief and the rest of the source substrate 1.

The power of the radiation may be chosen so that the heating of the material to be removed does not damage the neighbouring zones. It is furthermore possible to use any sort of ionic species that allow the implanted material to be fractured, such as commonly used hydrogen and/or helium.

Advantageously, the selective electromagnetic irradiation is carried out over the entire area of the negative to be recycled, whatever the inclination and position of the source, which is preferably a laser. The irradiation may also be swept over the edge face of the substrate, this being useful in the case where a layer is removed by implantation from an ingot. There is no longer any need to target a beam precisely at the interface between the regions 5 in relief and the surface region 6, as was sometimes the case in certain process of the prior art. To do this, the laser is moved so as to sweep at least once over the whole area of the source substrate 1. As the undamaged material is transparent to the irradiation at the wavelength chosen, it is possible to irradiate portions of the surface of the source substrate 1 several times.

Alternatively, the selective electromagnetic irradiation is carried out locally in the regions 5 in relief under the control of an optical device that detects the regions 5 in relief. This is because, since the damaged material of the weakened interface 2 and the undamaged material of the source substrate 1 have different optical absorptions, it is possible, via the difference in contrast, to see the zones of the area of the source substrate 1 in which the thickness of damaged material is larger than elsewhere. As may be seen in Figure 3, these zones are located at the base of the regions 5 in relief.

Thus the optical device, which may be a simple video camera, advantageously detects the regions 5 in relief by virtue of this principle.

By coupling such an optical device to the laser, it is possible to control the latter so that it emits selective electromagnetic irradiation only when it is aimed at zones 5 in relief. This embodiment enables, at low cost, time and energy savings since the laser is activated for much less time.

For III-N materials and in particular for GaN, which absorbs, when it is damaged, from a wavelength of 370 nm, or for SiC which absorbs, when it is damaged, from a wavelength of 415 nm, pulsed-mode doubled YAG (yttrium-aluminium-garnet) lasers configured to emit at a wavelength of 532 nm and/or with a power density of 0.1 to 2 J/cm^2 are preferred. It is also possible to use an argon laser that emits at a wavelength of 488 nm and 514 nm. A person skilled in the art will be able to choose from various types of lasers in order to tailor the wavelength and power density of the emission to any implanted source substrate 1.

Advantageously, the recycling process 200 comprises a second CMP (chemical-mechanical polishing) substep 220 after the selective electromagnetic irradiation.

This substep 220 makes it possible to finish the recycling of the source substrate 1 by treating the surface region 6 once the regions 5 in relief have been removed, in order to obtain a surface topology suited to a new use of the source substrate 1 as a donor substrate of a new thin layer 4. Detachment of this new layer 4 may be carried out after a step of depositing material on the substrate thus obtained, in order to renew the removed material and regenerate the initial thickness of the source substrate. This deposition may be carried out on the recycled surface of the negative (i.e. the surface exposed by the selective electromagnetic irradiation, optionally treated by CMP) or on the opposite side, called the back side. Since the layer 4 is not removed from the back side, the quality of the material is not important and the

deposition conditions can be less well controlled. When the contrary is the case, the deposited material will form the new layer 4 and the deposition method used will preferably be MBE (molecular beam epitaxy) or MOCVD (metal organic chemical vapour deposition) or HVPE (hydride vapour phase epitaxy) so as to provide a material with a good crystal quality.

The CMP polishing is a hybrid polishing operation which makes use of the combination of a chemical action and a mechanical force. A fabric, the "pad" is applied with pressure to the rotating surface of the material. A chemical solution, the "slurry", advantageously containing microparticles in suspension, typically colloids, is applied to the material. The slurry circulates between the surface and the pad and greatly increases the effectiveness of the polishing.

Preferably, the CMP polishing of step 220 uses a slurry comprising a colloidal acid solution enriched with diamond particles and/or an oxidizing agent.

The invention furthermore relates to a source substrate 1 recycled by such a process 200, and currently able to be reused in a new process for transferring a layer 4 to a support substrate 3 comprising again steps of:

- generating the weakened interface 2 in the recycled source substrate 1 at a depth bounding the thickness of the layer 4;
- bringing the recycled source substrate 1 and a support substrate 3 into contact; and
- fracturing heat treatment.

It is possible to envisage carrying out several transfer cycles and then recycling a source substrate 1, especially if the source substrate is still thick enough to provide the strength necessary for its manipulation and the compatibility necessary for use with production tools. Moreover, it is possible, as explained above, to reform the removed material on the recycled negative, by epitaxial growth for example, so

that the thickness of the source substrate remains constant. Material may also be deposited on the side opposite that used for the removal.

Example

On a self-supporting GaN source substrate 1 a layer of silicon oxide 500 nm in thickness was deposited. Hydrogen with a dose higher than 1×10^{16} atoms/cm^2 and an energy of 50 to 150 keV, depending on the thickness of the layer 4 to be transferred, was implanted into the GaN through the oxide layer. This led to an average species density of about 1×10^{21} atoms/cm^3 near the weakened interface 2 and the material became absorbent at a wavelength longer than or equal to 370 nm. In addition, a layer of 500 nm of silicon oxide was deposited on a sapphire support substrate 3.

The GaN and sapphire substrates were then brought into contact so as to bond them. Their surfaces can possibly be polished just before this contacting step - it is preferable for the RMS surface roughness measured by AFM (atomic force microscope) to be less than 5 ångströms over a 5 micron × 5 micron field (this field corresponding to the size of the observed zone).

RMS roughness means the root-mean-square roughness. It is a measurement consisting in measuring the value of the average squared deviation of the roughness. This RMS roughness therefore actually quantifies the average height of the peaks and troughs of the roughness, relative to the average height. This roughness is also monitored by AFM.

Once the substrates had been brought into contact, a heat treatment with a temperature increase to 200 to 700°C was carried out to strengthen the bond and cause the fracture in the implanted zone. The negative was recovered and the recycling begun.

The ring and the non-transferred zones on the surface of the negative of the GaN source substrate 1

were then removed by irradiation of the entire surface of the source substrate to be recycled at a wavelength of 532 nm with a "doubled YAG" laser, which is an yttrium-aluminium-garnet laser used in pulsed mode with a power density of 0.1 to 2 joules/cm^2. The unimplanted GaN, the crystal structure of which was not damaged, absorbs at a wavelength shorter than 365 nm. The absorption of the irradiation by the source-substrate negative at 532 nm is therefore selective.

CMP (chemical-mechanical polishing) finished the recycling, a colloidal acid solution provided with an additive such as diamond particles and/or an oxidizing agent can possibly be used. In order to be able to use this substrate in the same way as the initial substrate, it was necessary to polish it until scratches smaller than 15 nm in depth and an RMS roughness lower than 5 ångströms over a 20 micron × 20 micron field (measured by AFM) were obtained.

This substrate could once more be directly used in a process for detaching a layer but could also be used as a seed for epitaxial growth of a new material that restores the thickness of the initial substrate, before being used for the detachment of a new layer.

CLAIMS

1. Process for recycling a source substrate (1) comprising a surface region (6) and regions (5) in relief on the surface region (6), said regions (5) in relief corresponding to residual regions of a layer (4) of the source substrate (1), said residual regions not being separated from the rest of the source substrate (1) during a prior removal step implementing a separation at a weakened interface (2) formed by damaged material of the source substrate (1), the surface region (6) corresponding to part of the weakened interface (2) not separated from the rest of the source substrate (1) during the prior removal step, characterized in that it comprises selective electromagnetic irradiation of the source substrate (1) at a wavelength such that the damaged material of the surface region (6) absorbs the electromagnetic irradiation.

2. Process according to Claim 1, in which the regions (5) in relief correspond to a ring of material from the layer (4) of the source substrate (1) and/or to non-transferred zones of material from the layer (4) of the source substrate (1) distributed randomly on the surface region (6).

3. Process according to either one of Claims 1 and 2, in which the selective electromagnetic irradiation is carried out over the entire area of the source substrate (1).

4. Process according to either one of Claims 1 and 2, in which the selective electromagnetic irradiation is controlled by an optical device that detects the regions (5) in relief so that the irradiation is carried out locally on the regions (5) in relief.

5. Process according to Claim 4, in which said optical device detects the regions (5) in relief via the difference in optical contrast between the damaged material of the weakened interface (2) and the undamaged material of the source substrate (1).

6. Process according to one of the preceding claims, in which the source substrate (1) consists of a bulk material chosen from at least one of the following materials: SiC or a binary, ternary or quaternary III-N material; or consists of a composite structure of the GaNOS, InGaNOS, SiCOI or SiCopSiC type.

7. Process according to one of the preceding claims, in which the weakened interface (2) is generated by implanting ionic species (10) into the source substrate (1).

8. Process according to one of the preceding claims, comprising implementation of a chemical-mechanical polishing of the surface region (6) of the source substrate (1) following the selective electromagnetic irradiation.

9. Process according to Claim 8, characterized in that said chemical-mechanical polishing uses a colloidal acid solution enriched with an additive, in particular diamond particles and/or an oxidizing agent.

10. Process according to one of the preceding claims, in which the selective electromagnetic irradiation of the source substrate (1) is carried out by means of a laser.

11. Process according to Claim 10, in which the material of the source substrate (1) is GaN and the

laser emits at a wavelength longer than or equal to 370 nm.

12. Process according to Claim 10, in which the material of the source substrate (1) is SiC and the laser emits at a wavelength longer than or equal to 415 nm.

13. Process according to one of Claims 10 to 12, in which the laser is a pulsed-mode yttrium-aluminium-garnet laser.

14. Process according to Claim 13, in which the laser has a power density of 0.1 to 2 J/cm^2.

15. Process according to one of the preceding claims, comprising epitaxial growth of at least one layer of material on one surface of the source substrate (1).

16. Process according to the preceding claim, in which said epitaxial growth of material is carried out on the surface exposed following the selective electromagnetic irradiation.

17. Source substrate (1) recycled by a process according to one of the preceding claims so as to be reused.

18. Process for transferring a layer (4) from a source substrate (1) recycled according to Claim 13 to a support substrate (3) comprising steps of:

- generating a weakened interface (2) in the recycled source substrate (1) at a depth bounding the thickness of the layer (4);
- bringing the recycled source substrate (1) and a support substrate (3) into contact; and
- fracturing heat treatment.