# THIN FILM SPLITTING METHOD

The document US-5 374 564 discloses a method of fabricating thin films of semiconductor materials comprising the following steps:

(1) bombarding one face of the substrate with ions in order to implant those ions in a concentration sufficient to create in the substrate a layer of gas microbubbles forming microcavities defining a weakened layer;

(2) bringing this face of the substrate into intimate contact with a stiffener; and

(3) obtaining cleavage at the level of the microcavity layer by the application of heat treatment.

In the above document, the ions implanted in step 1 are hydrogen ions, but it is indicated that light ions of helium type or of other rare gases may also be used. As for the substrate, in the examples concerned it is formed of silicon, but it is indicated that it may also be a semiconductor from group IV of the periodic table of the elements, such as germanium, silicon carbide or silicon-germanium alloys.

In the above document, cleavage is obtained by means of heat treatment, but it is thereafter proposed, in variants of the method, to bring about cleavage by that kind of heat treatment and/or by applying a splitting stress (for example, by inserting a blade between the two substrates and/or by applying further traction and/or bending and/or shear forces and/or by further application of ultrasound or microwaves of judiciously chosen power and frequency).

It may be noted that the above method implies the formation of a weakening layer formed of microcavities resulting from gaseous species ions and that in practice it is light ions that are implanted. Implanting light ions has the advantage that implantation to significant

depths may be easily effected, but this is counterbalanced by the fact that these ions create few defects in the material so that it is therefore necessary to introduce them in large quantities to induce sufficient weakening (typically greater than $10^{16}$ or even $10^{17}$).

The paper "Ion implantation into GaN" by S.O. Kucheyev, J.S. Williams, S.J. Pearton in Materials Science and Engineering, 33 (2001) 51-107 and the paper "Ion implantation in GaN at liquid-nitrogen temperature: Structural characteristics and amorphization" by C. Liu, B. Mensching, M. Zeitler, K. Volz and B. Rauschenbach in Physical Review B of The American Physical Society, 1998, vol 57, N° 4, pp. 2530-2535, disclose that implanting Au or Ar ions in GaN has various advantages, in particular that it enables a well-defined impurity to be implanted at a well-defined depth in a substrate; in particular, it is therefore possible to effect precise doping or to insulate precise volumes electrically or to cause the localized formation of appropriate inclusions. However, experiments have been carried out to characterize the deterioration induced by this kind of implantation and to determine how to eliminate or at least minimize it.

One effect of implanting gold ions in GaN is the creation of crystalline disorder associated with the formation of microcavities that consist of "bubbles" of $N_2$ that result from the agglomeration of N atoms from the substrate. The passing implanted ions cause cascaded displacements of substrate atoms. These cascaded collisions induce a stoichiometric imbalance in the substrate: the heavier element (Ga in the case of GaN) is in excess at shallow depths while the deeper regions are enriched with the lighter element (N in the case of GaN). This effect increases in proportion to the mass of the ions implanted.

The invention tends to exploit this drawback.

**Definition of the invention**

It aims more precisely to exploit the degradation induced by the implantation of a non-gaseous heavy species in a substrate formed of at least two elements of which at least one is able to form a gaseous phase to bring about cleavage of the substrate to yield into a thin layer and a residual substrate.

It is worth noting that, although the technology described in the document US-5 374 564 cited above has been known for many years, including prior to the experiments concerning the implantation of Au ions in substrates such as GaN, it had not been realized that the degradation induced by this implantation could be exploited to the benefit of a cleavage function.

This may be explained by the fact that the cavities created by the implantation of a non-gaseous species do not contain implanted ions but molecules formed from one constituent element of the substrate in which the implantation has been effected, which is fundamentally different from the teaching of the document US-5 374 564 (or of documents that have considered variants of the method) in which the gaseous phase, if any, found in the microcavities is formed of implanted ions.

Furthermore, there is nothing to lead the person skilled in the art to think that the quantity of gas contained in the microcavities induced by the implantation of ions of a non-gaseous species could be sufficient for heat treatment or the application of a mechanical stress to be able to bring about cleavage.

Moreover, the degradation observed in the GaN because of implantation of Au ions was described as being distributed and dispersed within the volume (for example from the free surface of the substrates to a depth of a

few hundred nanometers), with the result that there was nothing that might lead the person skilled in the art to suppose that such degradation was nevertheless sufficient to weaken the substrate locally and to lead to a cleavage sufficiently well localized, in the case of heat treatment or the application of mechanical stress, to enable the formation of a thin layer usable afterwards.

In other words, the invention is based on the observation that this kind of implantation of ions of a non-gaseous heavy species in a substrate formed of at least two elements one of which is able to form a gaseous phase can also lead to cleavage similar to the cleavage observed in the technology described for the first time in the document US-5 374 564. The expression "heavy species" means a species having an atomic weight greater than 20, or even 40, or even 100.

Thus the invention proposes a method of fabricating thin films of semiconductor materials by implanting ions in any substrate composed of at least two different elements at least one of which can form a gaseous phase on bonding with itself and/or with impurities (residual or introduced, etc.). For example, the method may be applied to the following substrates: GaN, GaAs, a-Si :H, diamond, etc.

The method includes the following steps:

(1) bombarding one face of the substrate with ions of a non-gaseous heavy species in order to implant those ions in a concentration sufficient to create in the substrate a layer of microcavities containing a gaseous phase formed by the element of the substrate;

(2) bringing this face of the substrate into intimate contact with a stiffener; and

(3) obtaining cleavage at the level of the microcavity layer by the application of heat treatment and/or a splitting stress (for example, inserting a blade

between the two substrates and/or applying further traction and/or bending and/or shear forces and/or further application of ultrasound or microwaves of judiciously chosen power and frequency).

Accordingly, in the above method, and in contradistinction to the method described in the document US-5 374 564, the ions implanted in step 1 are not gaseous species: the ions implanted are any type of non-gaseous heavy ions (Au, W, Si, Ag, etc.). The effectiveness of the stoichiometric imbalance induced by this implantation is in direct proportion to the mass of the implanted ions: the greater the mass of the implanted ions, the lower the dose necessary to achieve cleavage.

In a variant of the method, there may be obtained after step 1 a region of microcavities that extends from the surface to a depth of a few tens or even hundreds of nanometers below the surface. There may therefore be obtained after implantation a surface film of a "structured" material consisting of a matrix (the initial material) and microcavities (voids, i.e. absence of material), i.e. a porous material. There may also be obtained a structured material consisting of a matrix and precipitates of implanted ions and/or elements of the initial material. This type of structured material may have advantageous optical and/or electrical and/or mechanical properties compared to the initial material (for example like porous Si compared to Si). It has nevertheless become apparent that, even if this region of microcavities extends from the surface to a certain depth, it is possible to bring about cleavage at a given depth, because there is always a depth such that the density and/or the size of the microcavities is at a maximum or such that the stress between the region of microcavities and the matrix is at a maximum. This depth defines the cleavage zone; the operating conditions for

obtaining this cleavage should be evident to the person skilled in the art, given his experience of the technology deriving from the document US-5 374 564.

Heat treatment may be carried out after implantation to cause the microcavities to evolve by diffusion/recombination and to increase the pressure of the gaseous phase.

To bring about cleavage, the structured material surface film may then be bonded to a stiffener (step 2). The cleavage step 3 is effected in the microcavity layer. The location and the width of the microcavity layer depend on the nature of the implanted ions, the implantation parameters (energy, dose, temperature, etc.), and the cleavage heat treatment, if any; the person skilled in the art knows how to select these parameters without any particular difficulties. Depending on the experimental conditions, the structured film may therefore be transferred in whole or in part to the stiffener.

Thus the general method of the invention may have the following advantageous features, separately or in combination:

- the substrate is a nitride (which gives rise to the formation of nitrogen within the substrate as a consequence of implantation); an instance of particular practical benefit is gallium nitride,

- the substrate is an arsenide; an instance of particular practical benefit is gallium arsenide,

- the substrate is a hydride (which gives rise to the formation of gaseous hydrogen as a consequence of the implantation); an instance of particular practical benefit is hydrogenated amorphous silicon $\alpha$-Si H,

- the substrate is essentially formed of carbon and contains a residual amount of impurities such as hydrogen (atomic quantity of the order of 1%); for

example, an instance of particular practical benefit is diamond,

- the implanted ion is a heavy metal ion; the implantation of gold ions is already well known in the art, but in accordance with the invention other ions may also be implanted, such as tungsten, silver, silicon or cesium,

- alternatively, the implanted ion is a non-metallic heavy ion, such as erbium, selenium or bismuth,

- the implanted ion is implanted at a dose from $10^{12}$ $cm^{-2}$ to $10^{16}$ $cm^{-2}$ with an energy from 2 MeV to 40 keV, respectively, the dose being adapted in particular as a function of the mass of the implanted ion and of the material to be implanted,

- cleavage is brought about by simple heat treatment,

- cleavage is brought about by at least one application of a splitting stress (where appropriate in addition to heat treatment); this stress may in particular be applied by inserting a blade between the two substrates and/or by applying further traction and/or bending and/or shear forces or further by means of ultrasound or microwaves of particular power and frequency.

Example 1

In a first example, a crystalline GaN ($^{70}Ga^{14}N$) substrate was implanted with Au ions under the following conditions: energy = 2 MeV, dose = $10^{16}$ $cm^{-2}$. There were obtained in this way spherical microcavities (bubbles of $N_2$) with controlled characteristics (dimensions = tens of nanometers, depth from the surface up to 400 nm below the surface with bubbles with a maximum size of around 250 nm). Porous GaN was formed in this way, which is a material that may have advantageous optical and/or electrical and/or mechanical properties compared to GaN.

The porous GaN substrate was then bonded by molecular adhesion to a stiffener (for example sapphire). For this purpose a layer of $SiO_2$ could be provided on the GaN substrate prior to implantation, for example. The sapphire substrate was also provided with a layer of $SiO_2$. This was followed by mechanical-chemical polishing and bringing the substrates into contact.

An appropriate heat treatment or annealing step (at a temperature from 200 to 1100°C) enables diffusion of the various atoms and/or species obtained after implantation and/or pressurization of the cavities to cause them to grow. This growth of the microcavities induces stresses and causes certain ones of them to coalescence, which leads to cleavage of the substrate at the level of the microcavity layer.

The thickness of the layer obtained was from 100 to 400 nm.

Example 2

In a second example, a wurtzite type crystalline GaN ($^{70}Ga^{14}N$) substrate was implanted with Au ions under the following conditions: energy = 300 keV, dose = $6 \cdot 10^{14}$ $cm^{-2}$. Lenticular microcavities were obtained in this way with controlled characteristics (dimensions = a few tens of nanometers, depth: up to 50 nm below the surface with a maximum cavity density 20 nm below the surface), the size and the density whereof were a function of the implanted dose. The GaN substrate structured and weakened in this way may then be subjected to a step of bringing it into intimate contact with a silicon stiffener by molecular bonding. The insertion of a blade, either alone in combination with heat treatment, for example carried out beforehand, leads to cleavage of the GaN substrate at the level of the microcavity zone. The above method may be used to produce thin films of "structured" GaN on silicon, for example, the thin film

consisting of the portion of the substrate remaining on the stiffener after cleavage.

Example 3

Tungsten was implanted in a Ga.As substrate, after which annealing heat treatment was applied at a temperature exceeding 450°C.

Example 4

Tungsten was implanted in an α-Si-H substrate.

CLAIMS

1. Method of fabricating thin films of semiconductor materials by implanting ions in a substrate composed of at least two different elements at least one of which can form a gaseous phase on bonding with itself and/or with impurities, the method comprising the following steps:

(1) bombarding one face of the substrate with ions of a non-gaseous heavy species in order to implant those ions in a concentration sufficient to create in the substrate a layer of microcavities containing a gaseous phase formed by the element of the substrate;

(2) bringing this face of the substrate into intimate contact with a stiffener; and

(3) obtaining cleavage at the level of the microcavity layer by the application of heat treatment and/or a splitting stress.

2. Method according to Claim 1, characterized in that the species of the ions and the implantation conditions are selected so that the layer of microcavities extends as far as the surface of the substrate.

3. Method according to Claim 1 or Claim 2, characterized in that the substrate is a nitride.

4. Method according to Claim 3, characterized in that the substrate is gallium nitride.

5. Method according to Claim 1 or Claim 2, characterized in that the substrate is an arsenide.

6. Method according to Claim 5, characterized in that the substrate is gallium arsenide.

7. Method according to Claim 1 or Claim 2, characterized in that the substrate is hydrogenated amorphous silicon.

8. Method according to Claim 1 or Claim 2, characterized in that the substrate is diamond.

9. Method according to any one of Claims 1 to 8, characterized in that the implanted ion is a heavy metal ion.

10. Method according to Claim 9, characterized in that the implanted ion is an Au, W, Ag, Si or Cs ion.

11. Method according to any one of Claims 1 to 8, characterized in that the implanted ion is an Er, Se or Bi ion.

12. Method according to any one of Claims 1 to 11, characterized in that the implanted ion is implanted at a dose from $10^{12}$ $cm^{-2}$ to $10^{16}$ $cm^{-2}$ with an energy from 2 MeV to 40 keV, respectively.

13. Method according to any one of Claims 1 to 12, characterized in that cleavage is brought about simply by heat treatment.

14. Method according to any one of Claims 1 to 13, characterized in that the cleavage is brought about at least by application of a splitting stress.

15. Method according to Claim 14, characterized in that the splitting stress is applied by inserting a blade between the two substrates and/or by applying further traction and/or bending and/or shear forces.

16. Method according to Claim 15, characterized in that the splitting stress is applied by means of ultrasound or microwaves of appropriate power and frequency.