MULTI-PURPOSE METALLIC SEALING

Field of the invention and prior art

The invention relates to the field of assembling thin layers and substrates.

In particular, it is applicable to the production of light-emitting diodes (LEDs) or laser diodes (LDs) with layer transfer by metal bonding.

The active layers of LEDs and LDs emitting in the green, blue or ultraviolet (constituted by GaN or AlGaInN alloys) are usually grown epitaxially on sapphire or SiC substrates (see, for example, the IEEE Journal On Selected Topics in Quantum Electronics, 8 (2002), 264, T. Mukai, "Recent progress in group-III nitride light emitting diodes", or Phys Stat Sol (a) 180 (2000) 5, V. Härle et al, "GaN-based LEDs and lasers on SiC"), while the active layers of LEDs or LDs emitting in the red, orange or yellow (constituted by GaAs or AlGaInP alloys) are essentially grown epitaxially on GaAs or InP substrates as described, for example, in the IEEE Journal on Selected Topics in Quantum Electronics 8 (2002) 321, K. Streubel et al "High brightness AlGaInP light emitting diodes". Said bulk substrates are selected principally for their physical properties: lattice parameters and thermal expansion coefficient suitable for the growth of active layers by epitaxy.

However, substrates such as silicon or certain metals would be preferable for the operation of the final device because of their better thermal conductivity (dissipation of the heat produced by the LED or LD in operation) and electrical conductivity (possibility of establishing a good electrical contact over the back face of the device opposite to the face used to extract the emitted light).

One known way of benefiting from those two types of substrates and their combined advantages consists of growing the active layers of the device on the first type

of substrate (sapphire, SiC or GaAs) then transferring that prefabricated device, by metal bonding, to a substrate adapted for the final steps of its fabrication and in particular to its optimum function. That transfer can be divided up into two critical steps: metal bonding of the final support to the active layers epitaxially grown on the initial substrate, then removal of the latter.

The laser lift-off separation technique described in United States patent US-A-6 071 795, for example, is a first known manner for removing the initial support used to grow the active layers after metal bonding. That technique consists of disintegrating the interface separating the initial substrate from the first thin layer reposing on the initial substrate using a laser, by illuminating starting structure from the back face. The disintegrated interface releases the thin layer from its support. That technique is limited to starting structures comprising an initial surface that is transparent to the laser beam and a first thin layer that absorbs the laser light. The only application of this technique appears to be that of detaching a thin layer of GaN epitaxially grown on sapphire.

N.W. Cheung et al (US-A-6 335 263) used a stack based on In and Pd to bond an LED structure based on GaN to a Si or GaAs substrate at 200°C. The starting sapphire substrate was detached by laser separation. Said Pd-In stack is unsuitable for mechanical release of a releasable substrate because of its poor mechanical strength. Further, the $PdIn_3$ layer formed does not constitute a good mirror for the LED light.

Other known means for removing the initial support consist of mechanical thinning (grinding or lapping) or chemical etching or a combination of mechanical thinning with chemical etching. Said methods remove the initial support but destroy it at the same time.

Mechanical thinning is particularly difficult with fragile substrates such as GaAs, and of long duration with hard substrates such as SiC, GaN, AlN or sapphire. Chemical attack is also of long duration and limited to substrates for which a solution (an acid) exists which can selectively etch the support and not the active layers epitaxially grown thereon. GaAs and Si are almost the only examples of an initial support in that case. Selective chemical etching of GaN, SiC, AlN and sapphire appears to be impossible.

As an example, K Streubel et al (see the article cited above) used an AuSn alloy to carry out metal bonding at 350°C of an LED structure based on GaAs to a Si substrate. The initial GaAs substrate, subsequently chemically etched, could not be recycled in that case as it had been destroyed.

In methods for fabricating LEDs developed by the Visual Photonics Epitaxy Co (described in US-A-6 287 882, for example), an AuBe alloy was used for metal bonding. Again, the method was not optimized economically, as the initial substrate was removed by chemical etching.

International patent WO-A-02/33760 discloses a method of producing LEDs on a composite substrate which is partially removed during the method. Proposed releasing methods include:

- chemical etching (destruction of the initial support), suitable for GaAs and Si, but not for SiC, GaN or sapphire;
- laser separation, limited to a transparent substrate such as sapphire, and unsuitable for Si, SiC supports.

In the method described in that document, motifs are produced in the active layers prior to application of the final support. That step for producing motifs by a combination of photolithography and etching is complex, expensive and renders the structure ensemble weak. In the case, not envisaged in that document, of mechanical

release of the initial support, the active layers cut into motifs would be a prime rupture zone. The release solutions proposed in WO-A-02/33760 are thus not universal (no release solution for SiC supports), and not inexpensive (recycling can only be envisaged with a sapphire support removed by laser separation); further, mechanical release is excluded by the type of structure proposed because the motifs render the active layers weak.

Further, that document also discloses the presence of a metallic mirror layer ensuring electrical contact. However, no precautions are taken to limit diffusion of metals into the active layers of the LED.

A further known means for removing the initial substrate consists of mechanically releasing the structure produced by epitaxial growth on a releasable substrate, i.e. a substrate formed from a support and a thin layer weakly adhering thereto. Several types of releasable substrates can be envisaged, for example of the type described in French patents FR-A-2 823 599 or FR-A-2 809 867.

That approach, necessitating the use of a releasable initial substrate, is relatively universal as regards the nature of the initial substrate and allows the initial support to be recycled after release. It is not limited to transparent substrates (as is the case with laser separation) or to materials that can be chemically etched. After separating the active layers from the initial support, the latter can be recycled and used again as a releasable substrate for epitaxial growth. However, the stresses inherent to mechanical release of the starting substrate require a strong bond between the active layers and the final substrate to prevent a fracture from occurring.

Thus, there is a problem with providing a method of producing a thin layer on a final substrate from a starting substrate which allows the latter to be recycled

(regardless of the nature), by dint of non-destructive mechanical release.

Regarding the device itself, there is currently no combination of layers between the final substrate and the active layers having the properties of ohmic contact, optical reflectivity and optionally electrical conductivity and/or mechanical strength.

Disclosure of the invention

In a first aspect, the invention provides a method of producing a thin layer of a semiconductor material on a substrate termed the final substrate, comprising:

- forming said layer of semiconductor material on a support termed the initial support;
- assembling said thin layer and said final substrate by metal bonding;
- mechanically separating the initial support from the thin layer.

The initial support comprises at least one surface film on which the thin layer of semiconductor material is formed, preferably by epitaxy, and a mechanical support. The initial support is termed releasable because of the presence of a weak interface between the layer of semiconductor material and the mechanical support.

Metal bonding can assemble the thin layer and the final substrate, and is both sufficiently mechanically strong and compatible with subsequent separation of the weak interface and not at the bonding interface without destroying the initial support.

Metal bonding is achieved using a stack of layers comprising at least one ohmic contact layer formed directly on the epitaxially grown layer of semiconductor material, a reflective layer and a layer based on gold or aluminium. The reflecting layer (mirror) is preferably based on silver, aluminium, rhodium, platinum or gold.

A supplemental layer can also be provided to act as a diffusion barrier. It is preferably based on tungsten, titanium, chromium, platinum or tantalum.

Metal bonding can be carried out using a metallic deposit partly formed on the thin layer and partly on the final substrate.

The final substrate can be a silicon substrate or a conductive substrate coated with a film of silicon.

After depositing the metal, assembly of the thin layer and the final support comprises a step for bringing the surfaces to be bonded into contact and heat treatment to form a eutectic phase alloying the silicon supplied by the final support and the gold or aluminium deposited as a thin layer at least on the layer of semiconductor material. The formation of Au-Si or Al-Si provides the good mechanical strength of the metal bond.

The stack of metallic layers ensures good thermal and electrical conduction between the final substrate and the thin layer of semiconductor material.

The mechanical separation step following assembly by metal bonding comprises separation along the weak interface initially present.

In accordance with one feature of the invention, the semiconductor material of the thin layer is an $Al_xGa_{1-x-y}In_yP$ or $Al_xGa_{1-x-y}In_yN$ alloy in which $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

The invention also concerns an intermediate substrate comprising a substrate and a thin layer of a semiconductor material connected via a metal bond.

Said intermediate substrate can then be used for the fabrication of a variety of components and in a variety of manners, in particular for the production optoelectronic devices such as LEDs, laser diodes, solar cells or photoreceptors.

In particular, contact pins can be formed on the thin layer of semiconductor material after the mechanical separation step. Said pins can be transparent and/or not

cover the entire surface of the layer of semiconductor material.

Brief description of the figures

Figures 1A to 1F describe steps in an implementation of the invention.

Detailed description of implementations of the invention

An implementation of the invention will now be given with reference to Figures 1A to 1F.

An example of an initial substrate is shown in Figure 1A. Said substrate is releasable in-type and comprises a surface film 102 acting as a support for epitaxial growth, connected to its support 101 via a weak interface or buried zone. This interface, which can be released mechanically, is designated by reference numeral 103. It allows non-destructive release of the substrate.

Said weak zone results, for example, from implantation of ionic or atomic species as described, for example, in FR-A-2 681 472 or EP-A-0 807 970, or by porosification as described in EP-A-0 925 888, or by molecular bonding with control of the hydrophilic nature and the roughness of the surfaces in contact at the weak zone, as described in FR-A-2 823 599.

In the case in which the active layers to be deposited are based on AlGaInN-type alloys, the surface layer 102 is preferably a layer of SiC or sapphire or Si, AlN or GaN. In contrast, if the active layers are based on AlGaInP-type materials, the surface layer is preferably formed from GaAs, Si or InP. In all cases, the surface layer is preferably monocrystalline.

After applying the active layers 104 by epitaxial growth, a first series of metallic deposits 105 is produced on the top of the active layers (Figure 1B). This first metallic stack can optionally be divided into a plurality of thin films of different natures.

The metal layer directly in contact with the active layers is, for example, a very thin layer (with a thickness in the range 1 nanometer (nm) to 50 nm, for example) ensuring both good mechanical adhesion (keying layer) and good ohmic contact with the semiconductor of the last active layer (low contact resistance). As an example, if the last active layer is constituted by p-type GaN, the contact can is preferably the stack Ni (5 nm) + Au (5 nm) or a layer of Pt (50 nm). If, however, it is p-type GaAs, a Zn/Au, Zn/Pd or Ti/Pt type contact would be suitable. Establishing good ohmic contact on the active layers 104 may necessitate heat treatment after application of the ohmic contact layer and prior to the metal bonding step.

Above the ohmic contact layer, the reflective layer (mirror) is deposited and is preferably based on: Ag, Al or Rh to produce a mirror in a spectral region such as the ultraviolet and/or blue and/or green, or Au, Ag, Al, Rh or Pt to produce a mirror in a spectral region such as yellow and/or orange and/or red and/or the infrared. Depending on the semiconductor constituting the last active layer, it may be that the ohmic contact is of the same nature as the reflective layer (for example: ohmic contact on p-GaAs constituted by zinc then gold (Zn/Au), then a mirror constituted by gold (Au), the mirror layer then being deposited in the continuity of the ohmic contact).

A diffusion barrier can also be established to limit the diffusion of metallic elements towards the active layers. Without taking this precaution, such an unwanted diffusion phenomenon would result in reducing the service life of the components produced. The barrier can be placed directly above the mirror deposited during the previous step, or it can be integrated into the ohmic contact if it is very thin. It is preferably based on W, Ti, Cr, Pt or Ta (pure and/or nitrided phase such as TiN, WN, etc).

The metal stack deposited can be terminated by a layer allowing strong bonding, namely a layer based on gold (or aluminium).

A further series of metal deposits 106 may be applied to the final support 107, preferably constituted by silicon, or by a conductive substrate coated with silicon.

A thin layer of Ti, Cr (with a thickness in the range 1 nm to 50 nm, for example) can then be directly applied to the deoxidized surface of the final support to ensure good adhesion and thus good mechanical behavior. A further layer of gold (or aluminium) can then finally be deposited with a view to metallic bonding. The nature of the metallic deposits 106 is selected to ensure ohmic electrical contact with the final support 107.

The method is continued by a metal bonding step (Figure 1C) during which the two metallized supports are brought into contact and bonded to each other, for example by dint of a heat treatment that may be carried out in a controlled atmosphere (vacuum, inert atmosphere, etc) and under mechanical pressure to reinforce the bond. The two supports are preferably bonded by the formation of a eutectic phase, for example Au-Si (the gold can be that of the metallizations adjacent to one or other of the supports, the silicon diffusing from the final support 107 entirely constituted by Si or having a deposit of Si at its surface). Eutectic Al-Si bonding can also be used, for example, despite the high temperature required: $T_{eutectic}$ (Al-Si) = 580°C > $T_{eutectic}$ (Au-Si) = 363°C, and also by taking care that the surfaces coated with aluminium do not oxidize before coming into contact.

The initial support 101 can then be detached, in particular mechanically (Figure 1D): the releasable substrate is released at the weak interface 103. The initial support is not destroyed and thus can be recycled to act again as a base for a new releasable substrate. A

preferred form of release consists of introducing a thin blade at the weak interface between the initial support and the active layers. Under the stress of said blade, a fracture propagates preferentially along the interface 103. The opening can also be assisted by a jet of fluid (inert or corrosive gas, water, etc).

A further form of release consists of applying a tensile force to the structure following metal bonding, for example by progressively distancing the initial support from the final support using grips and vacuum aspiration.

Prior to releasing, chemical cleaning (HF acid, aqua regia solution, etc), can be used to facilitate mechanical opening.

Following release, the film 102 used as the starting surface for epitaxial growth and optionally a portion of the active layers 104 can be removed by chemical-mechanical polishing or by chemical etching (applicable to a film of GaAs, Si), by plasma etching or ion beam etching (adapted to the majority of materials constituting the film 102, including inert and hard materials such as GaN, SiC, sapphire, AlN, etc). This etching step allows the epitaxially grown active layers 104 to be trimmed.

An intermediate substrate is obtained that can be used for the fabrication of LEDs or LDs or for solar cells or for photoreceptors. This product (Figure 1E) is interesting per se as it allows the fabrication of a variety of components in a variety of manners.

To produce components, one possible route consists of depositing an ohmic contact 108 on the face free of active layers (Figure 1F). If the semiconductor 104 denuded by etching is n-type GaN, the contact is preferably a Ti/Al stack or a transparent oxide conductor (for example: In_2O_3: Sn, alloys of ZnO and In_2O_3). However, if the semiconductor is n-type GaAs, the contact is preferably a AuGe/Au stack. The face on which said

contact is deposited is the face for extracting the light emitted by the component and so the contact is preferably transparent and/or does not coat the entire surface.

The method described above has many advantages:

- the initial support 101 used for epitaxial growth, which support may be very expensive, is not destroyed and thus can be recycled;
- mechanical release detaches any type of support, including SiC, GaN, for which chemical etching is impossible and plasma or ion beam etching is very lengthy. Detaching the initial support mechanically is not limited to transparent materials, as is the case with lift-off laser separation, nor to materials reacting to chemical attacks: it is a universal and inexpensive release means;
- the different metal layers used have all of the desired properties: ensuring both the functions of ohmic contact and a mirror, establishing good thermal conduction and electrical conduction between the support and the active layers without losing performance due to uncontrolled diffusion phenomena, and excellent mechanical behavior because strong materials are selected.

Some particular examples of implementations of the invention will now be given.

EXAMPLE 1: production of LEDs emitting in the blue-UV and based on AlGaInN

The releasable substrate used in this example was composed of a support 101 formed from polycrystalline SiC or silicon and a surface epitaxially grown layer 102 formed from 6H-SiC. Between these two portions were a buried layer of oxide and the releasable interface 103. The active layer based on GaN and AlGaInN alloys were epitaxially applied to film 102. The metal deposits 105 were then successively deposited on the active layers:

- Ni (thickness 5 nm) + Au (thickness 5 nm): ohmic contact to p-layer;
- Pt: as diffusion barrier;
- Ag: layer forming mirror;
- Au: for bonding

At the same time, a final support 107 was prepared for eutectic bonding by means of the following metallizations:

- Cr (thickness 5 nm): keying layer;
- Au: for bonding.

The metallized substrates were brought into contact under vacuum then heated to a temperature of close to 400°C under a slight mechanical pressure applied using a piston (P < 2 bar). A eutectic phase based on gold and silicon was formed, which resulted in a strong bond. After cooling, the bonded wafers were detached from each other using a thin blade introduced to the weak interface. The film 102 of 6H-SiC was removed by reactive ion etching (RIE). Finally, ohmic Ti/Al contact was produced on the n-GaN layer denuded by etching in accordance with the geometry shown in Figure 1F.

EXAMPLE 2: Production of an intermediate substrate for the fabrication of LEDs or LDs emitting in the red and based on AlGaInP

The releasable substrate used in this example was composed of a support 101 formed from Si and a surface epitaxially grown layer 102 formed from GaAs. Between these two portions were a buried layer of oxide and the releasable interface. The active layers based on GaS and AlGaInP alloys were applied epitaxially to the GaAs film. The metal deposits were then successively deposited on the active layers:

- Au/Zn: ohmic contact to p-layer;
- Ti: diffusion barrier;
- Au: layer forming mirror and permitting bonding;

At the same time, a final support 107 was prepared for eutectic bonding by means of the following metallizations:

- Ti (5 nm): keying layer;
- Au: for bonding.

The metallized substrates were brought into contact under vacuum then heated to a temperature of close to 400°C under a slight mechanical pressure applied using a piston (P < 2 bar). A eutectic phase based on gold and silicon was formed, which resulted in a strong bond. After cooling, the bonded wafers were detached from each other using a thin blade introduced to the weak interface, assisted by injection of a fluid.

The film 102 of GaAs was removed by chemical etching. A composite substrate was then obtained with active layers that were compatible with the fabrication of high performance LEDs or LDs since a mirror ohmic contact was already integrated over the whole surface of the active zone (reflection of the light emitted towards the support, optimum injection of current at the back face, etc).

EXAMPLE 3: Production of LEDs emitting in the green and based on GaN epitaxially grown on Si (111)

The releasable substrate used in this example was composed of a support 101 formed from Si and a surface epitaxially grown layer 102 formed from Si with crystallographic orientation (111). Between these two portions were a buried layer of oxide and the releasable interface 103. The active layers based on GaN and AlGaInN alloys were applied to Si film 102 or via a buffer layer based on AlN. The metal deposits were then successively deposited on the active layers:

- Ni/Cr/Au: ohmic contact to p-layer, with integrated Cr diffusion barrier;
- Au: mirror and bonding layer;

A final support 107 was prepared for eutectic bonding by means of the following metallizations:

- Cr (5 nm): keying layer;
- Au: bonding layer.

The metallized substrates were brought into contact under vacuum then heated to a temperature of close to 400°C under a slight mechanical pressure applied using a piston (P < 2 bar). A eutectic phase based on gold and silicon was formed, which resulted in a strong bond. After cooling, the bonded wafers were detached from each other using a thin blade introduced to the weak interface. The film 102 of Si was removed by chemical etching (TMAH). The optional AlN based buffer layer could also be removed by dry etching. Finally, an ohmic Ti/Al contact 108 was produced on the denuded n-GaN layer 104, as shown in Figure 1F.

In particular, the invention can allow:

- the production of light-emitting diodes or laser diodes, preferably based on GaN (and AlGaInN alloys) or on GaAs (and AlGaInP alloys);
- the production of an intermediate substrate comprising active layers of the components mentioned above (cf figure 1E).

CLAIMS

1. A method of producing a thin layer (104) of a semiconductor material on a substrate (107), termed the final substrate, said final substrate being a silicon substrate or a conductive substrate coated with a film of silicon, said method comprising:

- forming said layer of semiconductor material on a support termed the initial support (101);
- assembling said thin layer and said final substrate by metal bonding;
- producing a metal deposit (105, 106) on the thin layer and on the final substrate with a view to metal bonding;
- mechanically fracturing the initial support along a weak interface (103).

2. A method according to claim 1, in which said thin layer (104) is produced by epitaxial growth.

3. A method according to claim 2, in which the initial support comprises a substrate (101) and an epitaxially grown layer (102).

4. A method according to claim 3, in which the mechanical separation step comprises separating the ensemble along the weak interface.

5. A method according to any one of claims 1 to 4, in which metal bonding is achieved using a stack of layers (105, 106) comprising an ohmic contact layer, a reflective layer and a layer based on gold or aluminium.

6. A method according to claim 5, in which the reflective layer is based on silver, aluminium, rhodium, gold or platinum.

7. A method according to any one of claims 1 to 6, in which metal bonding involves the formation of a eutectic phase.

8. A method according to claim 7, in which the eutectic phase is Au-Si or Al-Si.

9. A method according to any one of claims 5 to 8, in which the stack of layers further comprises a layer forming a diffusion barrier.

10. A method according to claim 9, in which the diffusion barrier comprises tungsten, titanium, chromium, platinum or tantalum.

11. A method according to any one of claims 1 to 10, further comprising producing contact pins (108) on the semiconductor material layer after the mechanical separation step.

12. A method according to claim 11, in which the pins are transparent and/or do not cover the entire surface of the semiconductor material layer.

13. A method according to any one of claims 1 to 12, in which the semiconductor material of the thin layer (104) is an $Al_xGa_{1-x-y}In_yP$ or $Al_xGa_{1-x-y}In_yN$ alloy in which $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

14. An intermediate substrate comprising:

- a substrate (107) being a silicon substrate or a conductive substrate coated with a film of silicon and a thin layer (104) formed from a semiconductor material bonded via a metal bond (105, 106).

15. An intermediate substrate according to claim 14, in which the metal bond comprises a stack of metallic layers (105, 106).

16. An intermediate substrate according to claim 15, in which the stack of metallic layers comprises an ohmic contact layer, a reflective layer and a layer based on gold or aluminium.

17. An intermediate substrate according to claim 16, in which the reflective layer is based on silver, aluminium, rhodium, gold or platinum.

18. An intermediate layer according to claim 16 or claim 17, in which the stack of metallic layers further comprises a layer forming a diffusion barrier.

19. An intermediate layer according to claim 18, in which the diffusion barrier layer comprises tungsten, titanium, chromium, platinum or tantalum.

20. An intermediate layer according to any one of claims 14 to 19, further comprising contact pins (108) on the thin layer (104) of semiconductor material.

21. An intermediate layer according to claim 20, in which the pins are transparent and/or do not cover the entire surface of the semiconductor material layer.

22. An intermediate layer according to any one of claims 14 to 21, in which the semiconductor material of the thin layer (104) is formed from an $Al_xGa_{1-x-y}In_yP$ or $Al_xGa_{1-x-y}In_yN$ alloy in which $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

23. An optoelectronic device comprising an intermediate layer according to any one of claims 14 to 22.