



**PATENTTI- JA REKISTERIHALLITUS**

## Patenttikirja - Suomi

Patentti- ja rekisterihallitus on patenttilain nojalla  
myöntänyt oheisen patenttijulkaisun mukaisen patentin.

## Patentbrev - Finland

Patent- och registerstyrelsen har med stöd av patentlagen  
meddelat patent enligt bifogade patentskrift.

## Letters Patent - Finland

The Finnish Patent and Registration Office has, under the Finnish Patents Act,  
granted a patent disclosed in the accompanying patent specification.

Helsinki/Helsingfors 31.08.2020

A handwritten signature in blue ink, likely belonging to the Director General of the Patent and Registration Office.

Pääjohtaja/Generaldirektör/Director General

(19)



SUOMI - FINLAND

(FI)

PATENTTI- JA REKISTERIHALLITUS

PATENT- OCH REGISTERSTYRELSEN

FINNISH PATENT AND REGISTRATION OFFICE

(10) **FI 128613 B**

(12) **PATENTTIJULKAISU**

**PATENTSKRIFT**

**PATENT SPECIFICATION**

(45) Patentti myönnetty - Patent beviljats - Patent granted

**31.08.2020**

(51) Kansainvälinen patenttiluokitus - Internationell patentklassifikation - International patent classification

**H01L 29/861** (2006.01)

**H01L 33/30** (2010.01)

**H01L 31/0352** (2006.01)

**H01L 29/15** (2006.01)

**H01S 5/42** (2006.01)

(21) Patenttihakemus - Patentansökning - Patent application

20195617

(22) Tekemispäivä - Ingivningsdag - Filing date

**05.07.2019**

(23) Saapumispäivä - Ankomstdag - Reception date

**05.07.2019**

(43) Tullut julkiseksi - Blivit offentlig - Available to the public

**31.08.2020**

(32) (33) (31) Etuoius - Prioritet - Priority  
19.06.2019 FI 20195541

(73) Haltija - Innehavare - Proprietor

**1 •Comptek Solutions Oy**, Voimakatu 14, 20520 TURKU, SUOMI - FINLAND, (FI)

(72) Keksijä - Uppfinnare - Inventor

**1 •Lång, Jouko**, LIETO, SUOMI - FINLAND, (FI)

**2 •Tuominen, Marjukka**, RAISIO, SUOMI - FINLAND, (FI)

**3 •Dahl, Johnny**, TURKU, SUOMI - FINLAND, (FI)

**4 •Alonso, Vicente**, PIISPANRISTI, SUOMI - FINLAND, (FI)

(74) Asiamies - Ombud - Agent

**Moosedog Oy**, Rykmentintie 2B, 20810 Turku

(54) Keksinnön nimi - Uppfinningens benämning - Title of the invention

**VALOSÄHKÖINEN LAITE**

**Optoelektronisk anordning**

**OPTOELECTRONIC DEVICE**

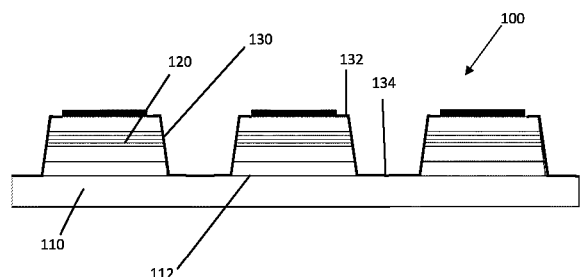
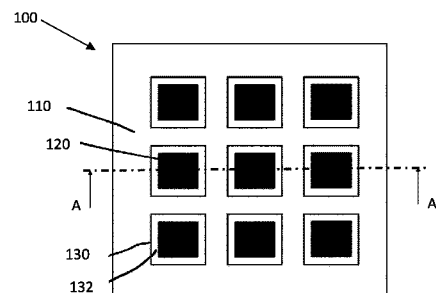
(56) Viitejulkaisut - Anförda publikationer - References cited

US 2018159005 A1, US 2006110839 A1, US 2004108530 A1, US 5807765 A, WO 2019020869 A1

(57) Tiivistelmä - Sammandrag - Abstract

Keksintö koskee optoelektronista laitetta (100, 200, 250, 260, 300) käsittäen substraattikerroksen (110, 210, 310, 107), ensimmäinen pintataso (112, 212, 105) ja toinen pintataso (214) vastapäätä ensimmäistä pintatasoa ja sen kanssa samansuuntaisesti. Laitte käsittää myös mesa-rakenteen (120, 220, 320, 820, 103, 123, 133), joka on järjestetty substraattikerroksen ensimmäiselle pintatasolle. Mesa-rakenne käsittää ainakin yhden kerroksen III-V materiaalia; ja ensimmäisen pinnan (101, 131), joka on järjestetty kulmaan  $\alpha$  suhteessa substraattikerroksen ensimmäiseen pintaan, jossa kulma  $\alpha$  on eri kuin  $0^\circ$  ja  $180^\circ$ . Laitte vielä lisäksi käsittää ensimmäistä tyyppiä olevan ensimmäisen pääteoksidikerroksen (130, 230, 330), joka on järjestetty mesa-rakenteen ensimmäiselle pinnalle.

The invention relates to an optoelectronic device (100, 200, 250, 260, 300) comprising a substrate layer (110, 210, 310, 107) having a first surface plane (112, 212, 105) and a second surface plane (214) opposite and parallel to the first surface plane. The device also comprises a mesa structure (120, 220, 320, 820, 103, 123, 133) arranged on the first surface plane of the substrate layer. The mesa structure comprises at least one layer of III-V material; and a first surface (101, 131) arranged at an angle  $\alpha$  with respect to the first surface plane of the substrate layer, wherein the angle  $\alpha$  is different from  $0^\circ$  and  $180^\circ$ . The device still further comprises a first terminating oxide layer (130, 230, 330) of a first type arranged on the first surface of the mesa structure.



## OPTOELECTRONIC DEVICE

### TECHNICAL FIELD

The present disclosure relates generally to an optoelectronic device and  
5 to a method for manufacturing an optoelectronic device. The  
optoelectronic device comprises a mesa structure.

### BACKGROUND

Optoelectronic devices such as lasers, light emitting diodes, detectors and  
photovoltaic devices typically consist of epitaxially grown semiconductor  
10 heterostructures including quantum well structures and more precisely  
compound semiconductor material-based structures. An example of the  
compound semiconductor material is a III-V compound semiconductor,  
which is obtained by combining group III elements (essentially Al, Ga,  
In) with group V elements (essentially N, P, As, Sb). In optoelectronic  
15 devices, a given semiconductor material is grown epitaxially as a layer on  
top of another given semiconductor material, thereby generating a  
heterostructure. Moreover, by using epitaxial-growth fabrication  
techniques, III-V semiconductors can be fabricated into quantum wells  
and similar stacked structures, for example for implementing light  
20 emitting diode (LED) structures. Furthermore, quantum wells are formed  
in semiconductors by having a material, such as indium gallium nitride  
(InGaN), sandwiched between two layers of a material with a wider  
bandgap, for example gallium nitride (GaN). Other possible examples of  
material combination may include layer of indium gallium aluminum  
25 phosphide (InGaAlP) sandwiched between two layers of indium gallium  
aluminum phosphide with higher aluminum concentration, and the like.  
These structures can be grown by processes like, molecular beam epitaxy  
(MBE) or metal organic chemical vapor deposition (MOCVD).

Furthermore, the epitaxially grown III-V compound semiconductor structures can be formed to mesa structures by using lithography techniques commonly known in the art by etching the semiconductor layer vertically. A mesa structure is a multilayer semiconductor structure formed on top of a substrate layer having a surface plane and oblique (or slanting) sides.

As an example of an optoelectronic device, photon generation in light emitting devices occurs in operation when charge carriers, confined between potential energy barriers induced by the band discontinuities, recombine to generate a photon. The photon has a wavelength that depends upon the energy difference between the quantum wells' corresponding conduction band minimum and valence band maximum; i.e. a band gap energy. Likewise, a photon detection occurs in photodetector devices in operation when a photon, with the higher energy than the band gap energy in the active region, is absorbed generating electron-hole pair that is subsequently collected with the voltage difference applied across the device.

In general, in optoelectronic devices, especially in light emitting devices, there is a requirement for efficient current injection into active quantum well regions of the optoelectronic devices. In a particular example of micro-LED devices, there is a poor device efficiency at the low injection current levels required to drive for instance a micro-led based display. In general, it would be desired that as high percentage as possible of the injected current is transferred to the light generation in the active regions of the devices and thus as many of the electrons injected should recombine with the holes and generate a photon. This is defined as internal quantum efficiency (IQE) of the LED.

The mechanism causing the poor efficiency is thought to be caused by several factors: (i) Shockley-Read-Hall (SRH) recombination of electrons/holes; (ii) Auger recombination; and (iii) electron overflow from

the quantum well. Notably, at the low current density operation of the device the main contribution to the IQE drop is caused by non-radiative Shockley-Read-Hall recombination at the defect states, thereby reducing light generation and output. Moreover, this recombination process generates excess heat which reduces the operating lifetime of a given optoelectronic device.

In the particular example of micro-LED devices, as the dimensions shrink, the LED surface-to-volume ratio increases and thus the material surface quality contributes in defining the final device performance. Namely, as the micro-LED mesa structure is processed using etching and lithography techniques, the LED's mesa sidewalls are characterized by high density of atomic level defects and structural disorder which are source for the defect states and the non-radiative SRH recombination and leakage current. Notably, in the example of micro-LED based display devices, as the charge carrier diffusion length can be comparable to the micro-LED size and pixel pitch, the impact of the defective sidewall can extend over large distances and can affect the performance of the entire volume of the chip.

The inherent source for the high density of defects in a typical compound semiconductor based optoelectronic device is the uncontrolled oxidation of the III-V material. The compound semiconductors' oxides are characterized by atomic level bond disorder, broken bonds (dangling bonds) and mixed group III and group V oxides. This nanometres thick oxide layer is prone to generate high density of electrically active defect states in the semiconductor material band gap. Especially group V oxides are prone to contribute to the high defect state density. The formation of such detrimental oxides is prone to happen during the processing of optoelectronic devices. In the particular example of micro-LED device mesa fabrication, after the mesa structure formation with lithography and etching techniques, the mesa surfaces are oxidized.

Contemporarily known semiconductor production facilities address the aforementioned problems, when fabricating optoelectronic device, by employing some known techniques. One such technique is to fabricate optoelectronic devices wherein there are employed chemical cleaning and passivation of the mesa side wall surfaces. Such a chemical passivation can be for example an ammonium sulfide based passivation or a SU-8 based passivation. A known problem with such passivations are that they are not stable and may oxidize easily. Another such approach is to deposit metal oxide overcoating (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ) onto mesa side walls using techniques such as atomic layer deposition (ALD), sputtering or plasma enhanced chemical vapor deposition (PECVD). These approaches for fabricating the optoelectronic devices are subject to generate a layer of poor-quality interface oxides and the associated defects as the overcoating materials contain oxygen and the chemical cleaning often is insufficient in removing oxides, especially in aluminum containing compound semiconductor materials.

Document US 2018/0159005 presents a light emitting device and method of forming the same, the light emitting device including a substrate, a buffer layer disposed on the substrate, a semiconductor mesa disposed on the buffer layer and including a first semiconductor layer, a light emitting active layer disposed on the first semiconductor layer, and a second semiconductor layer disposed on the first semiconductor layer, a contact layer disposed on an upper surface of the mesa, a passivation layer covering sidewalls of the mesa and the contact layer, and a cap structure including a reflective layer covering an upper surface of the contact layer, and a solder layer including a recess in which the reflective layer is disposed.

Therefore, in light of the foregoing discussion, there exists a need to overcome the aforementioned drawbacks associated with conventional semiconductor devices and conventional manufacturing techniques.

The present disclosure thus seeks to provide a solution to the existing problem of poor-quality optoelectronic device mesa surfaces with native oxide layer and the related non-radiative recombination and leakage current. An aim of the present disclosure is to provide a solution that overcomes at least partially the problems encountered in prior art, and provides an economical, easy to implement and sophisticated optoelectronic device.

#### SUMMARY OF THE INVENTION

The present disclosure seeks to provide an optoelectronic device. The present disclosure also seeks to provide a method of manufacturing an optoelectronic device.

The present disclosure provides an optoelectronic device comprising a substrate layer having a first surface plane and a second surface plane opposite and parallel to the first surface plane. The optoelectronic device further comprises a mesa structure arranged on the first surface plane of the substrate layer. The mesa structure comprises at least one layer of III-V material and a first surface arranged at an angle  $\alpha$  with respect to the first surface plane of the substrate layer, wherein the angle is different from  $0^\circ$  and  $180^\circ$ . The device still further comprises a first terminating oxide layer of a first type arranged on the first surface of the mesa structure. Furthermore, the first surface of the mesa structure has been cleaned by removing at least 75 % of native oxides on the first surface of the mesa structure before arranging the first terminating oxide layer of a first type thereon, and at least 50 % of the total oxide compounds of the first terminating oxide layer are group III oxides.

Present disclosure further provides a method for manufacturing an optoelectronic device, the method comprising

- obtaining a mesa structure arranged on a first surface plane of a substrate layer, the mesa structure comprising at least one layer of III-V

material and a first surface arranged at an angle  $\alpha$  with respect to the surface plane of the substrate layer, wherein the angle  $\alpha$  is different from  $0^\circ$  and  $180^\circ$ ;

- cleaning the first surface of the mesa structure by removing at least 75 % of native oxides on the first surface of the mesa structure; and
- forming a first terminating oxide layer of a first type on the first surface of the mesa structure.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The summary above, as well as the following detailed description of illustrative embodiments, is better understood when read in conjunction with the appended drawings. For the purpose of illustrating the present disclosure, exemplary constructions of the disclosure are shown in the drawings. However, the present disclosure is not limited to specific methods and apparatus disclosed herein. Moreover, those in the art will understand that the drawings are not to scale. Wherever possible, like elements have been indicated by identical numbers.

Embodiments of the present disclosure will now be described, by way of example only, with reference to the following drawings wherein:

FIG. 1A and 1B are schematic illustrations of an optoelectronic device according to a first embodiment of the present disclosure.

FIGs. 2A, 2B and 2C are schematic illustrations of an optoelectronic device, according to further embodiments of the present disclosure.

FIG. 3A is a schematic illustration of an optoelectronic device with native oxide on mesa structure surfaces.

FIG. 3B is a schematic illustration of an optoelectronic device with overcoating layer on top of a native oxide.

FIG. 3C is a schematic illustration of an optoelectronic device with terminating oxide layer according to a third embodiment of the present disclosure.

FIG. 3D is a schematic illustration of an optoelectronic device with terminating oxide layer and dielectric overcoating layer according to a fourth embodiment of the present disclosure.

FIG. 4 is a schematic illustration of a process flow according to a fifth embodiment of the present disclosure.

FIG. 5 is a schematic illustration of a processing equipment according to a sixth embodiment of the present disclosure.

FIG. 6 shows carrier lifetime decay curves, measured using time-correlated-single-photon counting, from a micro-LED device with native oxide and a micro-LED device processed according to a seventh embodiment of the present disclosure.

FIG. 7 shows photoluminescence spectra, illustrating a typical micro-LED device without passivation and with native oxide layer, a micro-LED device passivated using prior art techniques and a micro-LED device processed according to an eighth embodiment of the present disclosure.

FIG. 8 is a schematic illustration of vertical cavity surface emitting laser diode according to a ninth embodiment of the present disclosure.

FIG. 9A shows reflection-high-energy-electron diffraction pattern from a surface of InGaAlP material cleaned.

FIG. 9B shows reflection-high-energy-electron diffraction pattern from a surface of InGaAlP material passivated according to a tenth embodiment of the present disclosure.

FIG. 10A shows Ga2p X-ray photoelectron spectra from a micro-LED device with native oxide layer on the mesa surfaces.

FIG. 10B is Ga2p X-ray photoelectron spectrum from a micro-LED device with terminating oxide layer according to an eleventh embodiment of the present disclosure.

FIG. 10C is P2P X-ray photoelectron spectra from a micro-LED device with native oxide layer on the mesa surfaces.

FIG. 10D is P2P X-ray photoelectron spectra from a micro-LED device with terminating oxide layer according to a twelfth embodiment of the present disclosure.

FIG. 11 is a schematic illustration of an optoelectronic device according to a thirteenth embodiment of the present disclosure.

FIG. 12 is a schematic illustration of an optoelectronic device according to a fourteenth embodiment of the present disclosure.

FIG. 13 is a schematic illustration of an optoelectronic device according to a fifteenth embodiment of the present disclosure.

In the accompanying diagrams, an underlined number is employed to represent an item over which the underlined number is positioned or an item to which the underlined number is adjacent. A non-underlined number relates to an item identified by a line linking the non-underlined number to the item.

#### DETAILED DESCRIPTION OF EMBODIMENTS

The following detailed description illustrates embodiments of the present disclosure and ways in which they can be implemented. Although some modes of carrying out the present disclosure have been disclosed, those

skilled in the art would recognize that other embodiments for carrying out or practicing the present disclosure are also possible.

The present disclosure provides an optoelectronic device comprising a substrate layer having a first surface plane and a second surface plane  
5 opposite and parallel to the first surface plane. The optoelectronic device further comprises a mesa structure arranged on the first surface plane of the substrate layer. The mesa structure comprises at least one layer of III-V material and a first surface arranged at an angle  $\alpha$  with respect to the first surface plane of the substrate layer, wherein the angle is  
10 different from  $0^\circ$  and  $180^\circ$ . The device still further comprises a first terminating oxide layer of a first type arranged on the first surface of the mesa structure. Furthermore, the first surface of the mesa structure has been cleaned by removing at least 75 % of native oxides on the first surface of the mesa structure before arranging the first terminating oxide  
15 layer of a first type thereon, and at least 50 % of the total oxide compounds of the first terminating oxide layer are group III oxides

Present disclosure further provides a method for manufacturing an optoelectronic device, the method comprising

- obtaining a mesa structure arranged on a first surface plane of a  
20 substrate layer, the mesa structure comprising at least one layer of III-V material and a first surface arranged at an angle  $\alpha$  with respect to the surface plane of the substrate layer, wherein the angle  $\alpha$  is different from  $0^\circ$  and  $180^\circ$ ;
- cleaning the first surface of the mesa structure by removing at least 75  
25 % of native oxides on the first surface of the mesa structure; and
- forming a first terminating oxide layer of a first type on the first surface of the mesa structure.

The present disclosure thus provides a new method of passivating an optoelectronic semiconductor device by creating a terminating oxide layer  
30 on surfaces of the mesa structures of the optoelectronic device. Such

terminating oxide layer exhibits improved physical and electrical characteristics as compared to native oxides or other oxide layers formed or deposited by methods known heretofore. For these reasons such terminating oxide layer provides a beneficial passivating behavior suppressing the non-radiative recombination at the mesa structure surfaces with improved quality of the interface for subsequent dielectric overcoating deposition. Such terminating oxide layer thus provides an increase in energy barrier for the optoelectronic device for improving carrier confinement within the stacked configuration of the plurality of semiconductor layers formed as a mesa structure.

An optoelectronic device can refer to a device which is emitting photons or capable of detecting photons. Examples of such an optoelectronic device are a light emitting diode (LED), a micro-LED, a laser diode, a photovoltaic solar cell, and a photodetector. The present optoelectronic device may also be a part of a matrix of LED's, a matrix of photo detectors or multijunction solar cells. The optoelectronic device is thus a semiconductor device.

The optoelectronic device comprises a mesa structure arranged on top of a substrate layer having a surface plane. The mesa structure refers to isolated semiconductor stacks and comprises at least one layer of III-V material. Each isolated semiconductor stack functions as an optoelectronic component of the optoelectronic device. As an example, optoelectronic devices such as lasers, light emitting diodes, detectors and photovoltaic devices may consist of semiconductor heterostructures including active layers such as quantum well structures and more precisely compound semiconductor material-based structures. The semiconductor heterostructures are typically grown epitaxially on top of a substrate layer. An example of substrate layer is GaAs wafer. Another example of a substrate layer is an epitaxial III-V layer on a wafer. The surface plane of the substrate layer refers to for example (001) plane (in

cases of GaAs or epitaxial III-V layer on a wafer) or (0001) plane (in case of GaN).

The mesa structure (i.e. the isolated semiconductor stack) comprises a first surface arranged at an angle  $\alpha$  with respect to the first surface plane of the substrate layer. The angle between the surface plane and the first surface can be for example 30-90 degrees. The first surface is a surface which surrounds the mesa structure's sides, i.e. the sloping part. According to an embodiment, the mesa structure also comprises a second surface which is parallel to the first surface plane of the substrate layer. The second surface is the farthest away surface layer of the mesa structure from substrate. The surface layer refers to at least a first atomic layer of the structure.

The optoelectronic device further comprises a first terminating oxide layer of a first type arranged on the first surface of the mesa structure. In another embodiment a second terminating oxide layer of a second type arranged on the second surface of the mesa structure.

The first terminating oxide layer is arranged to surround the mesa structure, i.e. its sides. The first terminating oxide layer is of a first type. The first type is a terminating oxide layer which is group III oxide dominant. Group III oxide dominant refers to a situation where at least or more than 50 % of the total oxide compounds at the surface are group III oxides. It is noted that group V oxides and the related atomic bonds are prone to generate high density of defect states in the bandgap of the semiconductor and thus arranging the surface oxides to group III dominant oxides is intentioned. Furthermore, the first terminating oxide layer formed by the method of the present disclosure preferably exhibits a thickness lower than 10 nm. According to an embodiment, the composition (such as the level of dominance in percentage) and the thickness of the first terminating oxide layer depends on the materials present on a mesa sidewall, i.e. the first surface.

The second terminating oxide layer, when present, is arranged to cover the second surface of the mesa structure. The second terminating oxide layer is of a second type. In one embodiment, the second type is different from the first type. In another embodiment, the second type is identical to the first type. The second terminating oxide layer is preferably homogeneous in composition and thickness. In an alternative embodiment, the second terminating oxide layer is crystalline terminating oxide layer.

Thus, at least 50 % of the total oxide compounds of the first terminating oxide layer are group III oxides. According to another embodiment, at least 50 % of the total oxide compounds of the second terminating oxide layer are group III oxides. Thus, both the first and second or either of the first and second terminating oxide layers can be predominantly formed of group III oxides.

The mesa structures can be of any form, i.e. when seen from above (perpendicular to the first surface of the substrate layer), the mesa structure can have the form of a square, a rectangle, a circle or an ellipse, or any other suitable form. The mesa structure can have, when seen from the side, linear form, non-linear form, a combination of linear forms with different angles relative to the first substrate plane, a combination of non-linear forms, or a combination of linear and non-linear forms.

In an embodiment, where the optoelectronic device comprises a number of mesa structures (such as 2-10 or 10-50 or 50-100 mesa structures), these are preferably regularly arranged, or arranged according to a regular pattern (for example in a circle where the mesa structures close to the center of the circle are closer to one another than the mesa structures at the outer circle). The distance between adjacent mesa structures are indicated as a distance between the adjacent centers of mesa structures. The distance between centers of two adjacent mesa structures can be for example 2 - 500  $\mu\text{m}$  (micrometers). The distance

can be for example from 2, 4, 6, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 120, 150, 200, 250, 300 or 350  $\mu\text{m}$  up to 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 120, 150, 200, 250, 300, 350, 400, 450 or 500  $\mu\text{m}$ . According to one embodiment, the  
 5 optoelectronic device comprises a number of mesa structures, wherein the angle  $\alpha$  is larger than  $0^\circ$  and smaller than  $180^\circ$  and the distance between centres of two adjacent mesa structures is 2-500  $\mu\text{m}$ .

According to yet another embodiment, when the optoelectronic device comprises a number of mesa structures, a third terminating oxide layer  
 10 of a third type is arranged on a surface between two adjacent mesa structures. The third type of terminating oxide layer can be either identical than either the first or optional second terminating oxide layer, or it can be the same as the first and optional second terminating oxide layer, or it can be different from both the first and optional second  
 15 terminating oxide layer. It is also possible that only a first and third terminating oxide layers are present, without a second terminating oxide layer. The third type of terminating oxide layers may also be such that at least 50 % of the total oxide compounds are group III oxides. In this case, the surface is also preferably cleaned before forming the third  
 20 terminating oxide layer, by removing at least 75 % of native oxides on the surface of which the third terminating oxide layer is to be formed.

In an embodiment, the optoelectronic device may be micro-LED device. Indeed, the optoelectronic device may be a micro-light emitting diode, wherein the footprint of the mesa on the base layer is 1- 250000  $\mu\text{m}^2$ .  
 25 The footprint may be for example from 1, 10, 100, 500, 1000, 1500, 2000, 5000, 10000, 10500, 15000, 20000, 50000, 100000 or 150000  $\mu\text{m}^2$  up to 500, 1000, 1500, 2000, 5000, 10000, 10500, 15000, 20000, 50000, 100000, 150000, 200000 or 250000  $\mu\text{m}^2$ .

The footprint of the mesa on the base layer is defined as the parallel projection of the mesa structure (i.e. of a single mesa structure) onto the first surface plane of the substrate layer. The base layer in this description stands for that part of the device that is not covered by the mesa structures.

The term "micro" used here refers to the descriptive size of the device and in some embodiment may refer to individual component's lateral dimensions ranging from 1  $\mu\text{m}$  to 500  $\mu\text{m}$ . The sidewalls at the mesa structure of a typical micro-LED device are characterized by defects and associated non-radiative recombination centers for the injected charge carriers creating optically dead area surrounding the micro-LED device with low overall efficiency. This problem is avoided with the present application, thanks to the properties of the terminating oxide layers.

Indeed, the micro-LED device structure is passivated using processes to transform the micro-LED mesa surfaces including sidewall surfaces to terminating oxide layers with the characteristics of reduced amount defects and reduced non-radiative recombination and carrier leakage at mesa surfaces.

Yet in another embodiment, the optoelectronic device is a vertical cavity surface emitting laser (VCSEL), optionally where the minimum lateral dimension is 1  $\mu\text{m}$ . Indeed, the optoelectronic device may be a vertical cavity surface emitting laser, wherein the footprint of the mesa on the base layer is 1- 250000  $\mu\text{m}^2$ . The footprint may be for example from 1, 10, 100, 500, 1000, 1500, 2000, 5000, 10000, 10500, 15000, 20000, 50000, 100000 or 150000  $\mu\text{m}^2$  up to 500, 1000, 1500, 2000, 5000, 10000, 10500, 15000, 20000, 50000, 100000, 150000, 200000 or 250000  $\mu\text{m}^2$ . VCSEL devices may comprise mesa structures with multiple aluminum bearing Group III-V layers like AlGaAs and AlAs layers. The aluminum bearing layers may be protected from the environment in a

vertical direction by the top surface, which can include one or more surface passivation layers, i.e. terminating oxide layers. The aluminum bearing layers of known VCSEL devices are typically exposed to the environment at side surfaces of the mesa structures, particularly after the wafer has been cut into individual die. The native oxidation that happens in these materials is uncontrolled and the native oxide layer thickness increases from the edge inward of the aluminum bearing layers, eventually even reaching the VCSEL active layers, and thereby reducing performance or even preventing operation. VCSEL devices are commonly mounted in a hermetically sealed package that can be relatively expensive, and can be relatively bulky. These problems are avoided with the present devices, thanks to the first and optional second terminating oxide layers.

In another embodiment, the optoelectronic device is a photodetector. Indeed, the optoelectronic device may be a photodetector, wherein the footprint of one mesa on the base layer is  $1\ \mu\text{m}^2 - 100\ \text{mm}^2$ . The footprint can be for example from 1, 5, 50, 100, 250, 500, 700, 1000  $\mu\text{m}^2$ , 0.01, 0.1, 1, 10, 15, 20, 30, 35, 40, 45, 50, 55, 60, 65 or 70  $\text{mm}^2$  up to 50, 100, 250, 500, 700, 1000  $\mu\text{m}^2$ , 0.01, 0.1, 1, 10, 15, 20, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 100  $\text{mm}^2$ .

The photodetector typically comprises a multilayer stack of semiconductor materials such as InP, InGaAs, InGaAsP and GaAs, in any combination. The photodetectors typically have at least a p-n junction that converts photons into current which can be collected by applying a voltage across the p-n junction or additionally the photon absorption generates a voltage difference across the p-n junction. The absorbed photons make electron-hole pairs in the depletion region. Photodiodes and phototransistors are a few examples of photodetectors.

Moreover, the present disclosure concerns a new structure of vertically etched optoelectronics device with a terminating oxide layer covering the mesa structure surfaces.

In another aspect of the present disclosure a method for manufacturing an optoelectronic device is provided. The mesa structure is prefabricated (arranged) on the top of a substrate layer. The provided mesa structure which is arranged on top of the substrate layer is further processed by forming the first terminating oxide layer of the first type on the first surface of the mesa structure and optionally forming the second terminating oxide layer of the second type on the second surface of the mesa structure.

The method can be divided in three main steps; step S1 (preparation), step S2 (formation of first and optional second terminating oxide layer) and optional step S3 (overcoating). These are discussed in more detail below.

In the manufacturing method, the materials of the layers exposed in the first and optional second surfaces are prone to formation of a native oxide layer. This oxidation is preferably to be prevented to avoid efficiency decrease of the optoelectronic devices, due to the apparition of dark currents and current leakages caused by the native oxide layer, by mechanisms well known by people skilled in the art.

The method further comprises cleaning the first surface of the mesa structure by removing at least 75 % of native oxides on the first surface of the mesa structure. This is typically carried out in at least one cleaning step before forming the first terminating oxide layer. The various possible cleaning steps are explained in more detail below in connection with step S1.

According to an embodiment, the mesa structure comprises a second surface parallel to the first surface plane of the substrate layer, and the method further comprises forming a second terminating oxide layer of a second type on the second surface of the mesa structure. In this case, the second surface is also preferably cleaned before forming the second terminating oxide layer, by removing at least 75 % of native oxides on the second surface of the mesa structure.

The method may also comprise removing the substrate layer after forming the first terminating oxide layer and the optional second terminating oxide layer (and optional third terminating oxide layer). When such a step is used, the obtained optoelectronic device no longer comprises the substrate layer. It may optionally be placed on another substrate layer, and in case the angle  $\alpha$  was different from  $90^\circ$ , the angle  $\beta$  between the new substrate layer and the first surface of the mesa structure (i.e. the first surface comprising the first terminating oxide layer) is then naturally  $90^\circ - \alpha$ . The transferring of the mesa from one base layer to another can be done with means known in the art. A new surface of the mesa structure may be thus exposed (by removal of the substrate layer) and can be also treated to comprise a terminating oxide layer (which can be the same as one of the other terminating oxide layers or a different one).

Furthermore, the mesa structure can be formed (and not obtained ready-made). The formation of the mesa structure can be made with methods known in the art, for example Reactive Ion Etching (RIE). The etching depth to isolate mesa is selected beforehand. In an example, the material can be etched all the way to the substrate. In another example, the etching leaves material on the substrate between the mesas.

### Step S1

- In step S1 contaminants, carbon and native oxides are removed from the mesa structure(s). Removing is needed as those are detrimental when forming a first and optional second terminating oxide layer. It may be
- 5 that the substrate does not have any contaminants and carbon, but in case native oxides are present, at least 75 % of them are removed. According to an embodiment, at least 80%, 85 %, 90 %, 95 %, 96 %, 97 %, 98 %, 99 % or more of the native oxides are removed. It may even be that only a few ‰ of the native oxides remain after the cleaning.
- 10 According to an embodiment, the process begins with obtaining or providing a substrate with mesa structure formed on a substrate. During the step S1, a sequence of treatments is conducted to remove contamination, carbon and native oxides from the substrate comprising the mesa structure. In an embodiment, the contamination removal
- 15 consists of wet chemical treatment such as acetone-methanol-isopropyl alcohol treatment. In another embodiment, the contamination removal can be performed under ultrasonic agitation.

- In one embodiment, the carbon related atomic species are removed from the surfaces of the mesa structure, in a process step using a wet chemical
- 20 treatment. Such a process could be acetone-methanol-isopropyl alcohol treatment or additionally RCA cleaning. The details of the RCA cleaning are well known in the art. The treatments can be done under ultrasonic agitation. In another embodiment, the carbon removal step can be a dry cleaning process, such as oxygen plasma process. The oxygen plasma
- 25 generated for instance in down-stream remote plasma configuration is efficient in creating volatile carbon related species which are removed easily with vacuum pumps used in a plasma chamber configuration.

In an embodiment, after the carbon removal step, native oxides are removed. It is noted that the native oxides of III-V semiconductor exhibit

poor characteristics and contain high density of defects and associated electronic states in the semiconductor energy band gap. The native oxides comprise of mixture of group III and group V related oxides, dangling bonds and dimer bonds. Typically, the group V related oxides and the associated electronic states are considered harmful for the performance of the optoelectronic device. The effect of these oxides is shown below in relation to FIGs. 10.

In one embodiment of the native oxide removal, wet chemical treatment can be used. As an example, native oxides can be removed from different materials using chemicals such as hydrofluoric acid-based solutions, citric acid-based solutions or sulfuric acid-based solutions. For example, to clean mesa structures that contain materials like InGaAlP, GaAs, AlGaAs, InP, GaP, GaN, InGaN, a hydrochloric acid solution could be used. The molarity of the solution may vary from 0.1 M to 12 M depending on the material and the solvent may be deionized water, isopropyl alcohol or methanol. The etching time may vary from 1 s to 5 min depending on the chosen molarity of the solution as well as the material composition at the mesa structures. In order to avoid re-oxidation of the mesa surfaces after conducting such chemistry, the etching processes may be conducted in inert gas atmosphere whereas the partial content of oxygen in said environment is at least below 1000 parts-per-million (ppm). Other wet etching recipes that could also be used are hydrofluoric acid solutions. The hydrofluoric acid solution may be diluted using de-ionized water, buffered using a buffering agent such as ammonium fluoride. It is noted that in the wet chemical etching techniques, a chemical formulation may vary depending on the materials to be treated.

In another embodiment of the native oxide removal step, dry cleaning process could be used. In one embodiment, the dry native oxide removal process for the surfaces of the mesa structures is arranged for example using atomic hydrogen flux in vacuum conditions. The atomic hydrogen

flux can be generated, for instance using remote electron-cyclotron-resonance plasma source or by using hydrogen thermal cracker. A thermal cracker can dissociate the molecular hydrogen into atomic hydrogen. Yet another dry native oxide cleaning process is ion sputtering  
5 using noble gases.

According to an alternative embodiment, a dry process to perform the native oxide removal from the surfaces of the mesa structures is performed using ion bombardment such as sputtering utilizing noble gas atomic species such as helium, argon, neon or xenon. In such example,  
10 the ion source may be end-hall type gridless ion source with sufficiently low ion energy ( $<200$  eV) but yet high current density minimizing the sputtering damage and ion implantation to the mesa structure but allowing gentle removal of native oxides. In yet another example, the substrate may be biased to negative voltage during ion bombardment to  
15 increase the ion energy.

According to an embodiment, after the cleaning as described above (to remove contaminants, native oxides and carbon), the mesa is introduced to ultra-high-vacuum chamber conditions for step S2. By ultra-high-vacuum (UHV) it is meant here the vacuum of which base pressure  
20 conditions are within the range of  $1 \times 10^{-7}$  to  $1 \times 10^{-11}$  mbars.

### Step S2

In the first sub-step of S2, the optoelectronic device is heated to an elevated temperature in a degassing step in ultra-high vacuum conditions to essentially evaporate the volatile compounds left at the surfaces of the  
25 mesa structure from the previous cleaning steps. In one embodiment of the degassing step, the degassing temperature may vary from  $200^{\circ}\text{C}$  to  $600^{\circ}\text{C}$  depending on the materials at the mesa structure. It will be appreciated that a correct temperature and degassing time is required to promote the removal of volatile species from the cleaned mesa structure

surfaces. In one embodiment, the temperature can be chosen so that a light removal of group V atoms, such as arsenic and phosphorous, is achieved so that the first atomic layers at the first surface of the mesa structure becomes rich from group III elements.

- 5 After the degassing step is conducted, the mesa is processed to form the first terminating oxide layer. The mesa is controllably oxidized to form one or more terminating oxide layers on the surface of the mesa structure.

When the oxygen dose and surface temperature are selected correctly,  
10 the oxygen is absorbed into the surface and causes the transformation of the surface structure to good quality terminating oxide layer.

Indeed, in one embodiment, the oxidation conditions are chosen so that that the process promotes the generation of volatile group V oxides which are easily removed from the surfaces at elevated temperatures, thus  
15 making the first atomic layers at the surfaces of the mesa structures deficient from group V atoms and transforming the surfaces to good quality group III related oxides. The effect of removal of group V species can be monitored using for instance reflection high energy electron diffraction (RHEED), x-ray photoelectron spectroscopy (XPS) or  
20 monitoring by a mass-spectrometer during the degassing procedure. The effect of such treatment is explained in more detail below in connection with FIGs. 9.

In one embodiment, a metal deposition step is conducted prior the terminating oxide layer formation by evaporating for example 0.2-10  
25 monolayers (MLs) of In, Ga or Sn metals on the surfaces of the mesa structure resulting in group III or group IV rich surface layer. By conducting such metal deposition, the resulting surface is more susceptible for the formation of group V deficient terminating oxide layer.

According to an embodiment, the first terminating oxide layer is of a first type. The first type is a compound semiconductor oxide layer rich in group III oxides and with a thickness of less than 10 nm. More details are given in connection to FIGs. 9 and 10 below.

- 5 The optional second terminating oxide layer is of a second type. The second type depends on the processing conditions and geometries. The second type is a compound semiconductor oxide layer rich in group III oxides and with a thickness of less than 10 nm. Furthermore, if the planar surface of the structure has a crystal orientation of (001), the second  
10 terminating oxide layer may be crystalline terminating oxide layer.

As an example, the terminating oxide layers may be manufactured by employing an oxygen flux in vacuum conditions. The first and optional second terminating oxide layers can be fabricated by administering oxygen (as gaseous form, as  $O_2$  or  $O_3$ , or for example with  $H_2O_2$  being  
15 present) to heated surfaces of a mesa structure. Additionally, the administered oxygen may be generated at a plasma source which produces highly reactive atomic oxygen. Such plasma source may be electron-cyclotron-resonance plasma source installed remotely from the processed sample. When the oxygen dose and surface temperature are  
20 selected correctly, the oxygen is absorbed into the surface and causes the transformation of the surface structure into good quality terminating oxide layer. In one embodiment, the oxidation conditions are chosen so that the process promotes the generation of group V oxides which are highly volatile and easily removed from the surfaces at elevated  
25 temperatures, thus making the top most atomic layers at the surface of the mesa structures deficient from group V atoms and transforming the surfaces to good quality group III related oxides. Typically, only oxygen is used as a reagent, as compared to the more traditional oxide layer formation processes which typically involve using more than one element

reaction and where new oxide material is grown onto the surface instead of transforming the existing surface.

As a further example, an external surface of the mesa structure is heated to a temperature of at least 200 °C and up to 750 °C for supporting an oxidation process. The temperature is selected depending on the material composition of the external surfaces. The reaction typically takes place in vacuum conditions, with the chamber background pressure being typically in the range of  $1 \times 10^{-11}$  to  $1 \times 10^{-7}$  mbar. Subsequently, the external surfaces of the mesa structure are exposed to a flux of oxygen atoms, molecules, ozone or another oxidizer such as  $\text{H}_2\text{O}_2$  at the selected temperature. The partial pressure of oxygen during the oxidation process may vary from  $5 \times 10^{-8}$  to  $5 \times 10^{-3}$  mbar depending on the material composition of the treated mesa structure. Furthermore, the oxidation time may vary between 5 seconds and 60 minutes. In yet another embodiment, the terminating oxide layer is formed in an oxidation process under UV light irradiation under vacuum conditions. The UV irradiation can promote the formation of more reactive singlet oxygen quantum state for oxygen molecules during the oxidation process. Furthermore, the UV irradiation with short wavelength has an effect of breaking surface atomic bonds and thus promoting surface reactions. An example of a surface reaction promoting wavelength is 172 nm.

In an additional or alternative embodiment, indium atoms are deposited onto the mesa surfaces prior to transforming the surfaces to terminating oxide layers. Alternatively, tin atoms can be deposited onto the mesa surfaces prior to transforming the surface to a terminating oxide layer. In yet another example, gallium atoms are deposited onto the mesa surfaces prior to transforming the surface to terminating oxide layers. The deposition of metal atoms to the cleaned mesa surfaces has the effect of creating a thin group V deficient layer at the surfaces of the mesa structure to promote the formation of group III or additionally group IV

(Sn) related oxides during the terminating oxide layer formation. In such embodiments the deposition amount of metals is between 0.2 ML to 10 MLs (monolayers). For the deposition of such metal layers, thermal evaporator such as effusion cells or additionally electron beam evaporation may be used.

The process conditions for the creation of the terminating oxide layer may happen under UHV conditions, thus the process may happen under a free molecular flow regime where the mean free path of the molecules is larger than the size of the chamber where it takes place. Molecules can easily collide with any surface in the chamber. This characteristic allows the process to well conform to 3D surfaces.

After the terminating oxide layer formation step, the mesa structure is preferably cooled down to below 100 °C in UHV conditions in a cooling step.

### 15 Step S3

As an optional step, after the creation of the terminating oxide layer(s), the optoelectronic device can be transferred for the deposition of an overcoating. The overcoating deposition can be conducted for instance by using Chemical Vapour Deposition (CVD), ALD or PECVD or by sputtering deposition. Examples of overcoating layers are Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, SiN<sub>x</sub> or SiO<sub>2</sub>. A preferred process is to do the transfer via vacuum transfer lines in order to minimize the contamination absorption, although transfer by air has been also proven to provide good results. The transfer can also happen under UHV conditions or under high vacuum conditions or transferred through air or under inert gas environment.

In one embodiment, the vacuum transfer includes also a degassing step. After the overcoating deposition, post-annealing treatment such as rapid-thermal-annealing (RTA) can be done to improve the layer quality.

In such additional embodiment, there is provided a benefit of the creation of oxygen containing structures on mesa surfaces (the oblique side surfaces of the mesa structure) which are resistant to further oxygen exposure, and are characterized with low amount of atomic level defects.

5 The embodiments are suitable, for example, for optoelectronic and photovoltaic applications comprising quantum well (QW) semiconductor material structures formed as mesa structures. The semiconductor device typically comprises a stacked configuration of a plurality of semiconductor layers, such that the plurality of semiconductor layers is operable to  
10 accommodate charge carriers.

The beneficial effect of the terminating oxide layer(s) and its(their) passivating effect can be measured by assessing the minority carrier lifetime of the device. This measurement can be done for instance using time-correlated-single-photon-counting method thus addressing the time  
15 resolved photoluminescence characteristics of the device. Carrier lifetime is defined as the average time that it takes for a minority carrier to recombine. In a typical case with a material system with high density of defects, the minority carrier lifetime is short due to carrier loss due to non-radiative recombination. The effect of the terminating oxide layer is  
20 shown in connection with FIG. 6 below.

Additionally the effect of the terminating oxide layer can also be characterized by photoluminescence (PL) spectroscopy. In this technique, the microLEDs surfaces are excited by an external laser with a wavelength corresponding to an energy greater than the semiconductor  
25 material bandgap. After the excitation, the generated charge carriers recombine and in case of radiative recombination, the semiconductor material emits light. The intensity of photoluminescence is affected, among other things, by the amount of surface state defects created by for example poor quality oxides. In case of high density of defects, the  
30 SRH recombination is dominant and the photoluminescence intensity

emitted by the material is in general lower when compared to material with low density of defects. An example is shown in FIG. 7 below. The emission levels obtained with the devices that have terminating oxide layers are several times higher than same microLED devices which have  
5 been passivated with known passivation techniques.

In the manufacturing process the steps S1, S2 and S3 are typically done in separate chambers. These and other chambers can be isolated from each other with gate valves, which can allow the transfer of material through them when in open position. Additionally, the equipment will  
10 have different components to monitor and to produce different steps of the process S1, S2 and S3, such as pressure and temperature gages, heaters, vacuum pumps, plasma sources, plasma guns, sputtering heads, gas lines, leak valves etc.

In accordance with the present disclosure a method of passivating a  
15 semiconductor device comprising a stacked configuration of a plurality of semiconductor layers processed to form mesa structures, is provided. The plurality of semiconductor layers is operable to accommodate charge carriers, where the method consists in treating the mesa structures by first cleaning the exposed surfaces from carbon and contaminants, and  
20 secondly removing the native oxides (which hold bad electrical characteristics) and after that forming the said terminating oxide layer by a process with controlled conditions such as UHV conditions, substrate temperature, time, partial pressure of gases, and other, in a process that is conformable to 3D shapes.

25 In an embodiment a substrate was provided which contained a mesa structure with the first surface of the mesa comprising InAs. The surfaces of the mesa were cleaned from contamination and carbon with solvents. The used solvents were acetone, methanol and isopropyl alcohol. The sample was submerged in each solvent for 1 minute. The mesa was  
30 subsequently cleaned from native oxides with argon ion sputtering. The

ion gun filament current was 15 mA, ion gun voltage was 2 kV, the argon partial pressure was  $3 \times 10^{-6}$  mbar and the sputtering time was 15 min. The mesa was then introduced to a UHV chamber having background pressure  $1 \times 10^{-9}$  mbar. The mesa was degassed in UHV conditions with  
 5 annealing to 450 °C for 30 minutes. The obtained surface ready for oxidation showed (4x2) reconstruction under low energy electron diffraction measurement. Molecular oxygen gas was used as a reagent for the oxidation. The oxygen gas partial pressure was  $3 \times 10^{-6}$  mbar and the oxidation time was 15 min. The result was first terminating oxide  
 10 layer containing 90 % III-oxides and 10 % V-oxides.

Additional aspects, advantages, features and objects of the present disclosure would be made apparent from the drawings and the detailed description of the illustrative embodiments construed in conjunction with the appended claims that follow. It will be appreciated that features of  
 15 the present disclosure are susceptible to being combined in various combinations without departing from the scope of the present disclosure as defined by the appended claims.

#### DESCRIPTION OF THE DRAWINGS

FIG. 1A is a schematic illustration of an optoelectronic device **100** seen  
 20 from above, according to an embodiment. FIG. 1B is an illustration of a cross section A-A of the optoelectronic device **100**. The optoelectronic device **100** of the FIG. 1A comprises nine mesa structures **120**. Each mesa structure is arranged on a top of a substrate layer **110**, i.e. on its first surface plane. The first surface plane **112** of the substrate layer **110**  
 25 is indicated in FIG 1B. A first terminating oxide layer **130** of a first type is arranged on the first surface of the mesa structure **120**. As illustrated in FIG. 1A, the first terminating oxide layer **130** surrounds the mesa structure from all side directions. A second terminating oxide layer **132** is arranged on a second surface of the mesa structure **120**. The second  
 30 oxide layer **132** is parallel to the surface plane **112** of the substrate layer

**110.** In addition, a third terminating oxide **134** layer has been formed on top of the substrate layer, between the mesa structures.

FIGs. 2A, 2B and 2C are schematic illustrations of an optoelectronic device, according to further embodiments. In FIG. 2A, an optoelectronic device **200** includes a mesa structure **220** arranged on top of a substrate **210**, i.e. on its first surface plane. The first surface plane **212** is opposite and parallel to a second surface plane **214**. The mesa structure **220** comprises a first layer **202** (buffer layer in case of optoelectronic device being LED or micro-LED) epitaxially grown on top of the substrate, a second layer **204** grown on top of the first layer, an active region **206** grown on top of the second layer and a third layer **208** grown on top of the active region. A first terminating oxide layer **230** of the first type is arranged on the first surface of the mesa structure **220**. A second terminating oxide layer **232** of the second type is arranged on the second surface of the mesa structure **220**. Illustrative enlargement of the first surface is also provided in FIG. 2A. It can be seen that thickness of the first terminating oxide layer **230** varies depending on the material of the layer of the mesa structure. As seen in the illustrative enlargement, layer **206** comprises at its side a portion **240** of the terminating oxide layer which thickness is different than the thickness of a portion **242** that is arranged on the epitaxial layer **204**. The layer **208** comprises on its side a portion **244** of the terminating oxide layer which thickness is similar to the thickness of portion **240**. Furthermore, a contact **222** is formed on top of the third layer **208** and a third terminating oxide layer **234** is arranged on the surface of the substrate layer.

FIG. 2B shows another optoelectronic device **250** according to another embodiment. In this embodiment, a mesa structure **220** has been formed on the substrate **210**, but only its first surface has been treated to comprise the terminating oxide layer **230**. In FIG. 2C, yet another optoelectronic device **260** is shown, comprising a mesa structure **220**, a

first terminating oxide layer **230**, a second terminating oxide layer **232** and a third terminating oxide layer **234**. In this embodiment, the mesa structure has been manufactured such that the first layer **202** has been left on the substrate layer **210**, i.e. not etched away.

5 FIG. 3A is a schematic illustration of an optoelectronic device **300** with native oxide on mesa structure surfaces. A mesa structure **320** is arranged on top of a substrate **310**. The mesa structure **320** comprises a contact layer **322** fabricated for example using lithography techniques on top of the mesa structure **320**, and a native oxide layer **370** on top  
10 of the surfaces of the crystalline semiconductor material **360** of the mesa structure **320**. The native oxide layer **370** is also illustrated in the partial enlargement of FIG. 3A.

FIG. 3B is a schematic illustration of the optoelectronic device **300** with overcoating layer on top of a native oxide. A mesa structure **320** is  
15 arranged on top of a substrate **310**. The mesa structure **320** comprises a native oxide layer **370** on top of surfaces of the crystalline semiconductor material **360** of the mesa structure **320** and a dielectric layer **390** arranged on top of the native oxide layer **370**. The dielectric layer **390** is also illustrated in the partial enlargement of FIG. 3B.

20 FIG. 3C is a schematic illustration of the optoelectronic device **300** with terminating oxide layers according to a third embodiment of the present disclosure. A mesa structure **320** is arranged on top of a substrate **310**. The mesa structure **320** comprises a contact layer **322** fabricated for example using lithography techniques on top of the mesa structure **320**.  
25 Furthermore, a first terminating oxide layer **330** of the first type and a second terminating oxide layer **332** of a second type are arranged on the surfaces of the crystalline semiconductor material **360** of the mesa structure **320**, and a third terminating oxide layer **334** is arranged on the surface of the substrate layer **310**. The first terminating oxide layer  
30 **330** is also illustrated in the partial enlargement of FIG. 3C.

FIG. 3D is a schematic illustration of the optoelectronic device **300** with terminating oxide layers and dielectric overcoating layer according to a fourth embodiment of the present disclosure. A mesa structure **320** is arranged on top of a substrate **310**. The mesa structure **320** comprises a contact layer **322** fabricated using for example lithography techniques on top of the mesa structure **320**, a first terminating oxide layer **330** of the first type and a second terminating oxide layer **332** of a second type arranged on the surfaces of the crystalline semiconductor material **360** of the mesa structure **320**. a third terminating oxide layer **334** is arranged on the surface of the substrate layer **310**. In this illustration a dielectric overcoating **340** is arranged on top of the terminating oxide layers **330**, **332** and **334**. These are also illustrated in the partial enlargement of FIG. 3D.

FIG. 4 is an illustration of the process flow according to an embodiment of the present disclosure. The process flow describes the main process steps S1 (preparation), S2 (formation of the terminating oxide layer) and S3 (overcoating). The process begins with providing a substrate with patterned mesa structure formed on a substrate **400**. During the step S1, a sequence of treatments **402**, **404** and **406** are conducted to remove contamination, carbon and native oxides. In this embodiment the contamination removal **402** consists of wet chemical treatment such as acetone-methanol-IPA treatment. In one embodiment of the carbon removal process **404**, a wet chemical treatment is used, such as acetone-methanol-isopropyl alcohol treatment or additionally RCA cleaning. In another embodiment the carbon removal step **404** will be conducted using dry cleaning processes such as oxygen plasma process. After the carbon removal step **404**, native oxides are removed in step **406**. In one embodiment of the native oxide removal **406**, wet chemical treatment **410** will be used, such as hydrochloric or hydrofluoric acid-based treatment. In another embodiment of the native oxide removal step **406**, dry cleaning process **408** will be used such as atomic hydrogen treatment

or ion sputtering using noble gases. After the native oxide removal step **406**, the cleaned patterned substrate with mesa structures is introduced to ultra-high-vacuum chamber in step **412** of S1. A degassing step **414** of cleaned mesa structures is then made in a controlled manner by

5 annealing the mesa structures between 200 °C to 600 °C. After degassing step **414**, in one embodiment a metal deposition step **416** is conducted by evaporating 0.2-10 MLs of In, Ga or Sn metals on the surfaces of the mesa structure resulting in group III or group IV rich surface layer. Terminating oxide layer is arranged in step **418** either after

10 the degassing step **414** or after the metal deposition step **416**. In one embodiment, the terminating oxide layer is arranged in step **418** by administering oxygen (as gaseous form, as O<sub>2</sub> or O<sub>3</sub>, or for example with H<sub>2</sub>O<sub>2</sub> being present) to heated surfaces of the mesa structures. After the terminating oxide layer formation step **418**, the mesa structure can

15 optionally undergo a post oxide formation high temperature anneal step **420**. Additionally, the mesa structure can undergo a UV activation step **422**. At step **424** the mesa is cooled down below 100 °C in ultra-high-vacuum conditions in step **424**. After cooling the mesa structure in step **424**, transfer to overcoating equipment is conducted in step **426** of S3.

20 The transfer can happen under ultra high vacuum conditions or under high vacuum conditions in step **428** or transferred through air or under inert gas environment. In one embodiment the UHV transfer includes also degassing step in **428**. Subsequently, dielectric overcoating is deposited in step **430**, for instance using atomic layer deposition, plasma enhanced

25 chemical vapor deposition or by sputtering deposition. After the dielectric overcoating deposition, post-annealing treatment can be done in step **432**.

FIG. 5 is a schematic illustration of processing equipment according to an embodiment of the present disclosure. The processing equipment

30 comprises a glove box **510**, where wet preparation processes can take

place under inert controlled atmosphere, i.e. nitrogen atmosphere with oxygen concentration of less than 100 ppm. The glove box **510** is connected to a transfer chamber **520**, where a transfer mechanism to move the devices from the glove box to a different part of the equipment is mounted, for example a robot, or in another example a linear transfer rod system. The transfer chamber allows sample transfer with the required vacuum level between the chambers. The transfer chamber is connected to a buffer chamber **530** that connects the transfer chamber **520** and the oxidation chamber **540** and which allows a necessary high vacuum level to be achieved for the transferring of the sample to the terminating oxide layer formation chamber **540**. The reason for the buffer chamber is to compensate the different pressure levels required for the different steps, for example pressure in oxidation chamber **540** could be in the level of  $10^{-10}$  mbar, while in the transfer line **520** could be for example  $10^{-6}$  mbar. By adapting the pressure in the buffer chamber **530**, which is significantly of smaller volume than the other chambers, the process time is reduced. The transfer chamber **520** is also connected to an overcoating deposition chamber **550** where the deposition of the dielectric materials can take place. The overcoating chamber **550** can be for instance atomic layer deposition chamber or plasma enhanced chemical vapor deposition chamber.

FIG. 6 is an illustration a charge carrier lifetime decay curve, measured using time correlated single photon counting method, from standard micro-LED device with native oxide layer at the micro-LED mesa structure surfaces, and a lifetime decay curve from micro-LED device with terminating oxide layer at the micro-LED mesa structure surfaces. Both devices are based on InGaAlP based microLED arrays of sizes below 5  $\mu\text{m}$ . The carrier lifetime is defined as the average time that it takes to a minority carrier to recombine. In typical case with a material system with high density of defects the minority carrier lifetime is short due to carrier

loss due to non-radiative recombination. In FIG. 6, the device with terminating oxide layer shows that the carrier lifetime is improved substantially. In the FIG., lifetime (in ns) is shown on the abscissa and the counts (in absolute units) on the ordinate. The triangles show the results for a standard microLED ( $\langle\tau\rangle$  approximately 2.8 ns) and the circles the results for a microLED comprising the terminating oxide layers according to the present invention ( $\langle\tau\rangle$  approximately 3.5 ns).

FIG. 7 is an illustration of a photoluminescence spectrum from a standard micro-LED device with native oxide layer at the micro-LED mesa structure surfaces (lowest curve), and a photoluminescence spectrum from a micro-LED device wherein the micro-LED mesa structure surfaces are passivated using prior-art techniques (middle curve), and a photoluminescence spectrum from a micro-LED device with terminating oxide layer at the micro-LED mesa structure surface according to an embodiment of the present disclosure (uppermost curve). The wavelength (in nm) is shown on the abscissa and the photoluminescence intensity (in counts) on the ordinate. The devices were microLEDs based on InGaAlP material, of 10  $\mu\text{m}$  in size, and reference to the lower, middle and uppermost curve is to be seen in the middle of the graph.

FIG. 8 is an illustration of vertical cavity surface emitting laser (VCSEL) structure **800** according to an embodiment. A plurality of semiconductor layers **812** and **814** is arranged on top of a substrate **810**. In this example, the semiconductor layers **812** are the layers comprised in the bottom distributed Bragg reflector (DBR), and the layer **814** is an n-contact layer. The mesa structure is arranged on top of the n-contact layer **814**. In this example, the mesa structure comprises a plurality of layers that constitute n-type DBR **826**, optical microcavity **824**, oxide aperture layer **816**, p-type DBR **822** and a top p-type contact layer **818**. In this example the top dielectric DBR **828** is formed by plurality of layers of dielectric material. A first terminating oxide layer **830** of the first type

is arranged on the first surface of the mesa structure **820**. A second terminating oxide layer **832** of the second type is arranged on the second surface of the mesa structure. A third terminating oxide layer **840** is arranged on top of the n-contact layer **814**.

- 5 Such terminating oxide layers provide an increase in energy barrier for the semiconductor device for improving carrier confinement within the stacked configuration of the plurality of semiconductor layers formed as a mesa structure. The terminating oxide layer prevents the uncontrolled oxidation of the surfaces present in **822**, **826**, **816**, **818** and **824**  
 10 providing a passivating effect. These could eliminate the need for enclosing such devices in hermetically sealed packages.

FIG. 9A is an illustration of a reflection high energy electron diffraction pattern from a clean InGaAlP(001) material surface, cleaned as explained above. The diffraction pattern shows long range order of the surface with  
 15 (2x4) surface symmetry (another azimuth not shown) indicating that the surface is successfully cleaned from native oxides and other contaminants and the surface is reconstructed to form clean (2x4) surface symmetry as an example.

FIG. 9B is an illustration a reflection high energy electron diffraction  
 20 pattern from a InGaAlP(001) material surface with terminating oxide layer which is crystalline, according to the present disclosure. The diffraction pattern shows long range order of the surface with (3x1) surface symmetry in the planar (001) surface (another azimuth not shown), i.e. the terminating oxide layer is crystalline.

25 FIG. 10A is an illustration of a Ga2p x-ray photoelectron (XPS) spectra emission spectrum from an InGaAlP material based mesa structure with native oxide layer. The deconvoluted emission spectrum shows a component **1010** characteristics of Ga-O bonds. Furthermore, a

component **1012** is characteristic for a bonding environment of Ga in the host semiconductor stack.

FIG. 10B is an illustration of a Ga2p x-ray photoelectron emission spectrum from an InGaAlP material-based mesa structure with terminating oxide layer according to an embodiment of the present disclosure. The deconvoluted emission spectrum shows a component **1020** characteristic of Ga-O bonds which is much smaller compared to case with native oxide layer. Furthermore, a component **1022** is characteristic for a bonding environment of Ga in the host semiconductor stack.

FIG. 10C is an illustration of a P2p x-ray photoelectron emission spectrum from an InGaAlP material-based mesa structure with native oxide layer. The deconvoluted emission spectrum shows a weak component **1030** characteristic for P bonds within the host semiconductor material and an intense component **1032** indicating the oxidized phosphorous.

FIG. 10D is an illustration of a P2p x-ray photoelectron emission spectrum from an InGaAlP material-based mesa structure with terminating oxide layer, according to an embodiment. The deconvoluted emission spectrum shows a clear component **1040** characteristic for P bonds within the host semiconductor material. The component **1042** characteristic for phosphorous oxides is below detection limit of the XPS instrument.

FIG. 11 is a schematic illustration of a side view of an optoelectronic device similar to that shown in FIGs. 1A and 1B, according to an embodiment. It shows the angle  $\alpha$  between the first surface **101** of the mesa structure **103** and the first surface plane **105** of the substrate layer **107**. The line with reference number **109** shows the distance between centres of two adjacent mesa structures.

FIG. 12 is a schematic illustration of an optoelectronic device according to a fourteenth embodiment of the present disclosure. In this embodiment, the first surface of the mesa structure **123** is in two parts, namely **121a** and **121b**, which are arranged at an angle with respect to one another. The angle  $\alpha$  is measured as indicated in the FIG., i.e. along the active region **125** of the mesa structure.

FIG. 13 is a schematic illustration of an optoelectronic device according to a fifteenth embodiment of the present disclosure. In this embodiment, the first surface **131** of the mesa structure **133** is partly spherical, and the angle  $\alpha$  is measured as indicated in the FIG, i.e. along the active region **135** of the mesa structure.

Modifications to embodiments of the present disclosure described in the foregoing are possible without departing from the scope of the present disclosure as defined by the accompanying claims. Expressions such as "including", "comprising", "incorporating", "have", "is" used to describe and claim the present disclosure are intended to be construed in a non-exclusive manner, namely allowing for items, components or elements not explicitly described also to be present. Reference to the singular is also to be construed to relate to the plural.

## CLAIMS

1. An optoelectronic device (100, 200, 250, 260, 300) comprising
  - a substrate layer (110, 210, 310, 107) having a first surface plane (112, 212, 105) and a second surface plane (214) opposite and parallel to the first surface plane;
  - a mesa structure (120, 220, 320, 820, 103, 123, 133) arranged on the first surface plane of the substrate layer, the mesa structure comprising
    - at least one layer of III-V material; and
    - a first surface (101, 131) arranged at an angle  $\alpha$  with respect to the first surface plane of the substrate layer, wherein the angle  $\alpha$  is different from  $0^\circ$  and  $180^\circ$ ;
  - a first terminating oxide layer (130, 230, 330) of a first type arranged on the first surface of the mesa structure,

**characterised** in that the first surface of the mesa structure has been cleaned by removing at least 75 % of native oxides on the first surface of the mesa structure before arranging the first terminating oxide layer of a first type thereon, and that at least 50 % of the total oxide compounds of the first terminating oxide layer are group III oxides.
2. An optoelectronic device (100, 200, 250, 260, 300) according to claim 1, wherein the mesa structure (120, 220, 320, 820, 103, 123, 133) further comprises a second surface (132) parallel to the first surface plane (112, 212, 105) of the substrate layer (110, 210, 310, 107) and a second terminating oxide layer (132, 232, 332, 832) of a second type arranged on the second surface of the mesa structure.
3. An optoelectronic device (100, 200, 250, 260, 300) according to claim 1 or 2, wherein it is a micro-light emitting diode, and wherein a footprint of the mesa structure (120, 220, 320, 820, 103, 123, 133) on the substrate is 1- 250000  $\mu\text{m}^2$ .

4. An optoelectronic device (100, 200, 250, 260, 300) according to claim 1 or 2, wherein it is a photodetector, and wherein a footprint of the mesa structure (120, 220, 320, 820, 103, 123, 133) on the substrate is  $1\ \mu\text{m}^2$  -  $100\ \text{mm}^2$ .
- 5 5. An optoelectronic device (100, 200, 250, 260, 300) according to claim 1 or 2, wherein it is a vertical cavity surface emitting laser, and wherein a footprint of the mesa structure (120, 220, 320, 820, 103, 123, 133) on the substrate is 1-  $250000\ \mu\text{m}^2$ .
6. An optoelectronic device (100, 200, 250, 260, 300) according to any  
10 of the claims 2-5, wherein at least 50 % of the total oxide compounds of the second terminating oxide layer (132, 232, 332, 832) are group III oxides.
7. An optoelectronic device (100, 200, 250, 260, 300) according to any  
15 of the claims 2-6, wherein the second terminating oxide layer (132, 232, 332, 832) is a crystalline terminating oxide layer.
8. An optoelectronic device (100, 200, 250, 260, 300) according to any  
20 of the preceding claims, comprising a number of mesa structures (120, 220, 320, 820, 103, 123, 133), wherein the angle  $\alpha$  is larger than  $0^\circ$  and smaller than  $180^\circ$  and the distance between centres of two adjacent mesa structures is 2-500  $\mu\text{m}$ .
9. An optoelectronic device (100, 200, 250, 260, 300) according to claim 8, wherein a third terminating oxide layer (134, 234, 334, 840) of a third type is arranged on a surface between two adjacent mesa structures (120, 220, 320, 820, 103, 123, 133).
- 25 10. An optoelectronic device according to any of the preceding claims, wherein the angle  $\alpha$  is  $30^\circ$ - $90^\circ$ .

11. A method for manufacturing an optoelectronic device (100, 200, 250, 260, 300), the method comprising

- obtaining a mesa structure (120, 220, 320, 820, 103, 123, 133) arranged on a first surface plane (112, 212, 105) of a substrate layer (110, 210, 310, 107), the mesa structure comprising
  - at least one layer of III-V material, and
  - a first surface (101, 131) arranged at an angle  $\alpha$  with respect to the surface plane of the substrate layer, wherein the angle  $\alpha$  is different from  $0^\circ$  and  $180^\circ$ ;
- cleaning the first surface of the mesa structure by removing at least 75 % of native oxides on the first surface of the mesa structure; and
- forming a first terminating oxide layer (130, 230, 330) of a first type on the first surface of the mesa structure.

12. A method according to claim 10, wherein the mesa structure comprises a second surface (132) parallel to the first surface plane (112, 212, 105) of the substrate layer (110, 210, 310, 107); and the method further comprises forming a second terminating oxide layer (132, 232, 332, 832) of a second type on the second surface of the mesa structure (120, 220, 320, 820, 103, 123, 133).

13. A method according to claim 10 or 11, further comprising removing the substrate layer (110, 210, 310, 107) after forming the first terminating oxide layer (130, 230, 330) and the optional second terminating oxide layer (132, 232, 332, 832).

## PATENTTIVAATIMUKSET

1. Optoelektroninen laite (100, 200, 250, 260, 300) käsittäen

- substraattikerroksen (110, 210, 310, 107), jossa on ensimmäinen pintataso (112, 212, 105) ja toinen pintataso (214) ensimmäistä

5 pintatasoa vastapäätä ja samansuuntaisesti sen kanssa;

- mesa-rakenteen (120, 220, 320, 820, 103, 123, 133), joka on järjestetty substraattikerroksen ensimmäisen pintatason päälle, mesa-rakenteen käsittäessä

- ainakin yhden kerroksen III-V materiaalia; ja

10 - ensimmäisen pinnan (101, 131), joka on järjestetty kulmaan  $\alpha$  suhteessa substraattikerroksen ensimmäiseen pintatasoon, jossa kulma  $\alpha$  on eri kuin  $0^\circ$  ja  $180^\circ$ ;

- ensimmäistä tyyppiä olevan ensimmäisen pääteoksidikerroksen (130, 230, 330), joka on järjestetty mesa-rakenteen ensimmäiselle pinnalle,

15 **tunnettu** siitä, että mesa-rakenteen ensimmäinen pinta on puhdistettu poistamalla ainakin 75 % mesa-rakenteen ensimmäisellä pinnalla olevista luonnollisista oksideista ennen kuin sen päälle järjestetään ensimmäistä tyyppiä oleva ensimmäinen pääteoksidikerros, ja että ainakin 50 % kaikista ensimmäisen pääteoksidikerroksen oksidiyhdisteistä on ryhmän  
20 III oksideja.

2. Patenttivaatimuksen 1 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa mesa-rakenne (120, 220, 320, 820, 103, 123, 133) lisäksi käsittää toisen pinnan (132), joka on samansuuntainen kuin substraattikerroksen (110, 210, 310, 107) ensimmäinen pintataso (112,  
25 212, 105), ja toista tyyppiä olevan toisen pääteoksidikerroksen (132, 232, 332, 832), joka on järjestetty mesa-rakenteen toiselle pinnalle.

3. Patenttivaatimuksen 1 tai 2 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa se on mikrometriluokan valoa emittoiva diodi,

ja jossa mesa-rakenteen (120, 220, 320, 820, 103, 123, 133) jalanjälki substraatin pinnalla on 1-250000  $\mu\text{m}^2$ .

4. Patenttivaatimuksen 1 tai 2 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa se on fotodetektor, ja jossa mesa-rakenteen  
5 (120, 220, 320, 820, 103, 123, 133) jalanjälki substraatin pinnalla on 1  $\mu\text{m}^2$  - 100  $\text{mm}^2$ .

5. Patenttivaatimuksen 1 tai 2 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa se on pintasäteilevä laser, jossa on pystysuuntainen kaviteetti, ja jossa mesa-rakenteen (120, 220, 320,  
10 820, 103, 123, 133) jalanjälki substraatin pinnalla on 1-250000  $\mu\text{m}^2$ .

6. Jonkin patenttivaatimuksista 2-5 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa ainakin 50 % kaikista toisen pääteoksidikerroksen (132, 232, 332, 832) oksidiyhdisteistä on ryhmän III oksideja.

15 7. Jonkin patenttivaatimuksista 2-6 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa toinen pääteoksidikerros (132, 232, 332, 832) on kiteinen pääteoksidikerros.

8. Jonkin edellisistä patenttivaatimuksista mukainen optoelektroninen laite (100, 200, 250, 260, 300), käsittäen määrän mesa-rakenteita (120,  
20 220, 320, 820, 103, 123, 133), joissa kulma  $\alpha$  on suurempi kuin  $0^\circ$  ja pienempi kuin  $180^\circ$  ja kahden vierekkäisen mesa-rakenteen keskikohdan välinen etäisyys on 2-500  $\mu\text{m}$ .

9. Patenttivaatimuksen 8 mukainen optoelektroninen laite (100, 200, 250, 260, 300), jossa kolmatta tyyppiä oleva kolmas pääteoksidikerros  
25 (134, 234, 334, 840) on järjestetty pinnalle kahden vierekkäisen mesa-rakenteen (120, 220, 320, 820, 103, 123, 133) väliin.

10. Jonkin edellisistä patenttivaatimuksista mukainen optoelektroninen laite, jossa kulma  $\alpha$  on  $30-90^\circ$ .

11. Menetelmä optoelektronisen laitteen (100, 200, 250, 260, 300) valmistamiseksi, menetelmän käsittäessä sen, että

- 5 - aikaansaadaan mesa-rakenne (120, 220, 320, 820, 103, 123, 133), joka on järjestetty substraattikerroksen (110, 210, 310, 107) ensimmäiselle pintatasolle (112, 212, 105), mesa-rakenteen käsittäessä
  - ainakin yhden kerroksen III-V materiaalia, ja
  - ensimmäisen pinnan (101, 131), joka on järjestetty kulmaan  $\alpha$
- 10 suhteessa substraattikerroksen pintatasoon, jossa kulma  $\alpha$  on eri kuin  $0^\circ$  ja  $180^\circ$ ;
- puhdistetaan mesa-rakenteen ensimmäinen pinta poistamalla ainakin 75 % mesa-rakenteen ensimmäisellä pinnalla olevista luonnollisista oksideista; ja
- 15 - muodostetaan ensimmäistä tyyppiä oleva ensimmäinen päateoksidikerros (130, 230, 330) mesa-rakenteen ensimmäiselle pinnalle.

12. Patenttivaatimuksen 10 mukainen menetelmä, jossa mesa-rakenne käsittää toisen pinnan (132), joka on samansuuntainen kuin  
 20 substraattikerroksen (110, 210, 310, 107) ensimmäinen pintataso (112, 212, 105); ja menetelmä lisäksi käsittää sen, että muodostetaan toista tyyppiä oleva toinen päateoksidikerros (132, 232, 332, 832) mesa-rakenteen (120, 220, 320, 820, 103, 123, 133) toiselle pinnalle.

13. Patenttivaatimuksen 10 tai 11 mukainen menetelmä, joka lisäksi  
 25 käsittää sen, että poistetaan substraattikerros (110, 210, 310, 107) sen jälkeen, kun ensimmäinen oksidipäatekerros (130, 230, 330) ja valinnainen toinen oksidipäatekerros (132, 232, 332, 832) on muodostettu.

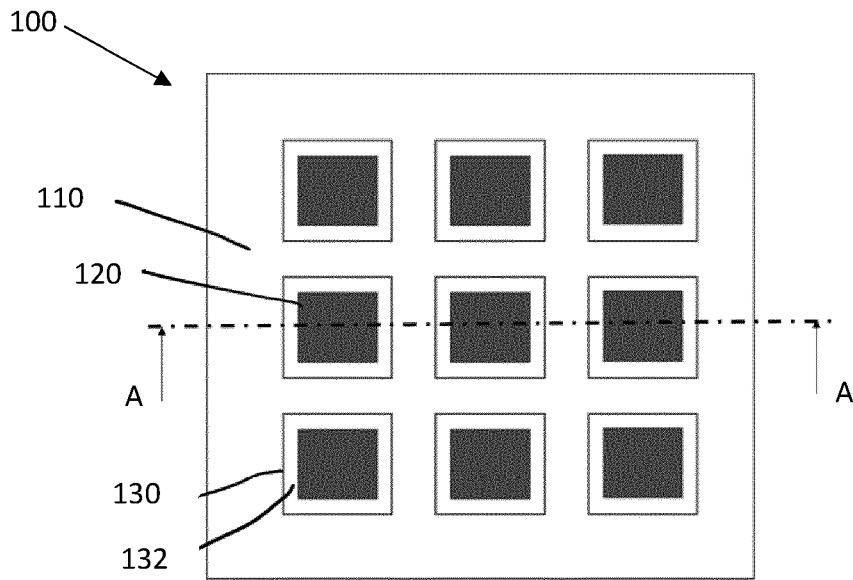


Fig. 1A

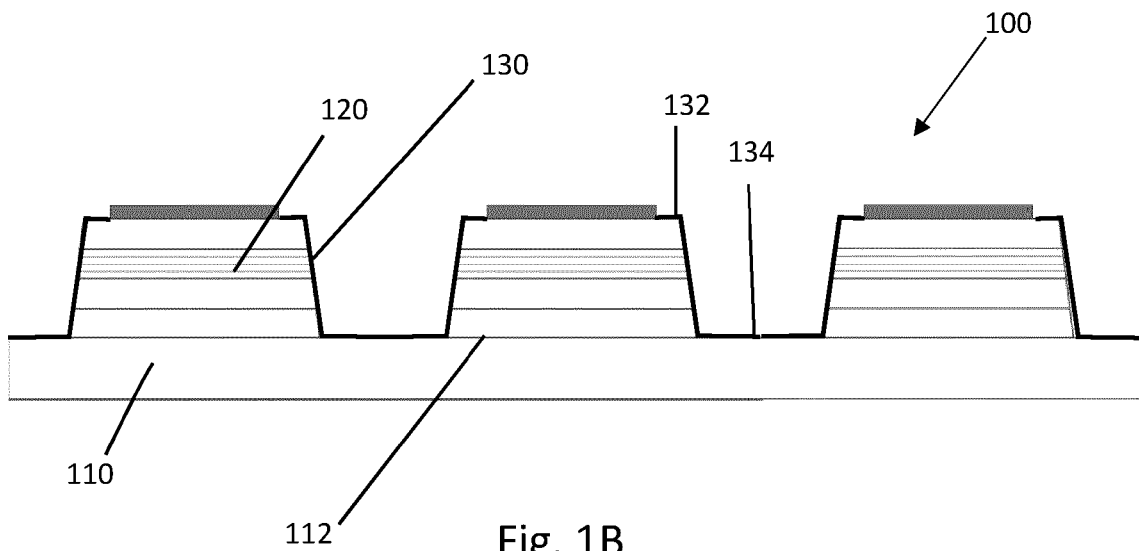
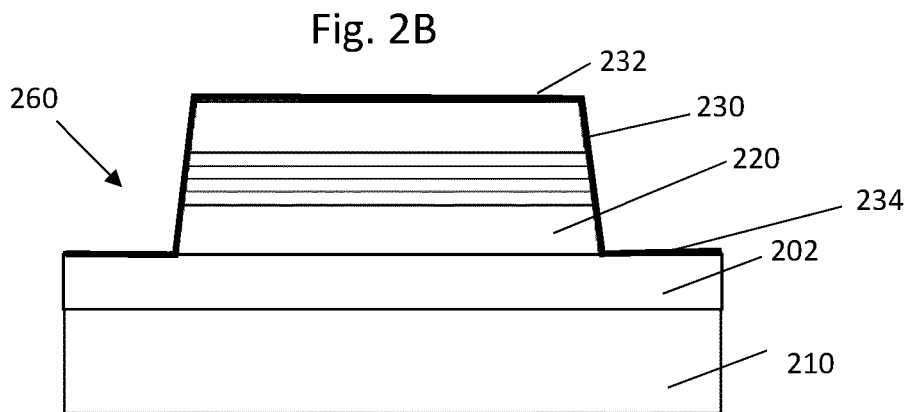
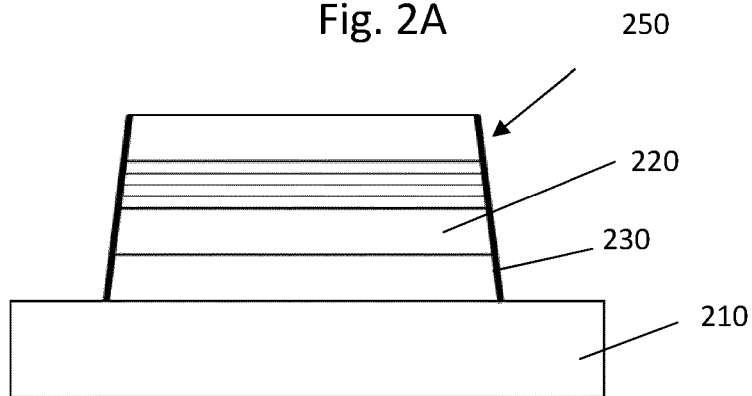
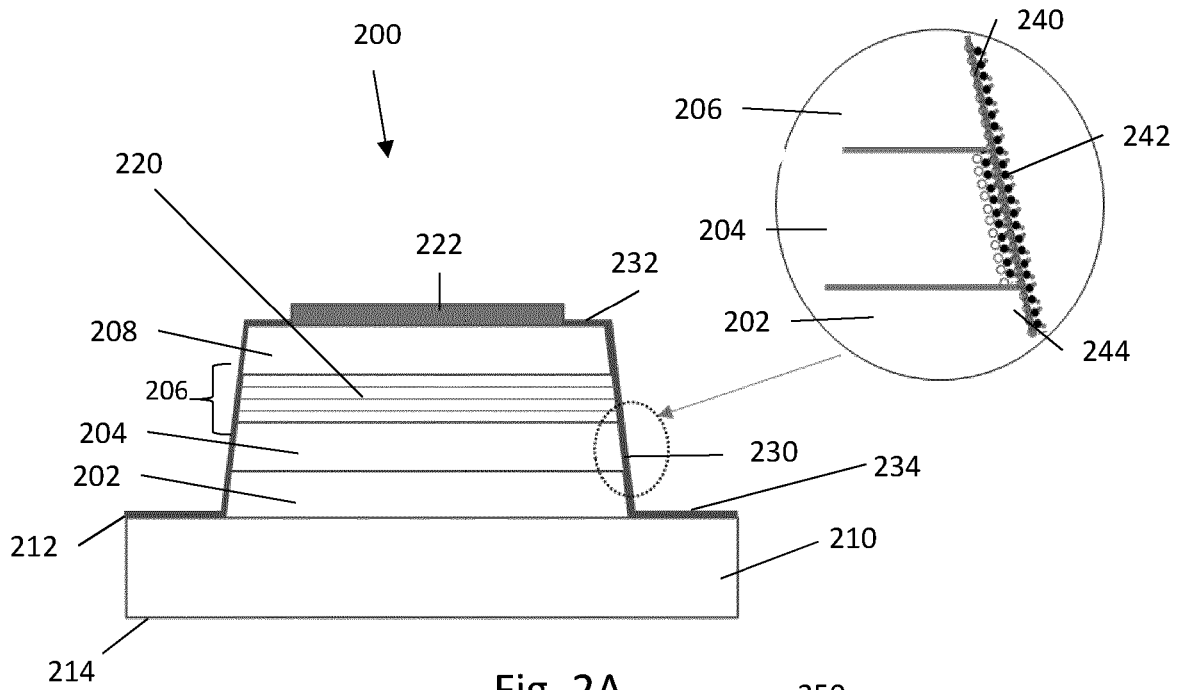


Fig. 1B



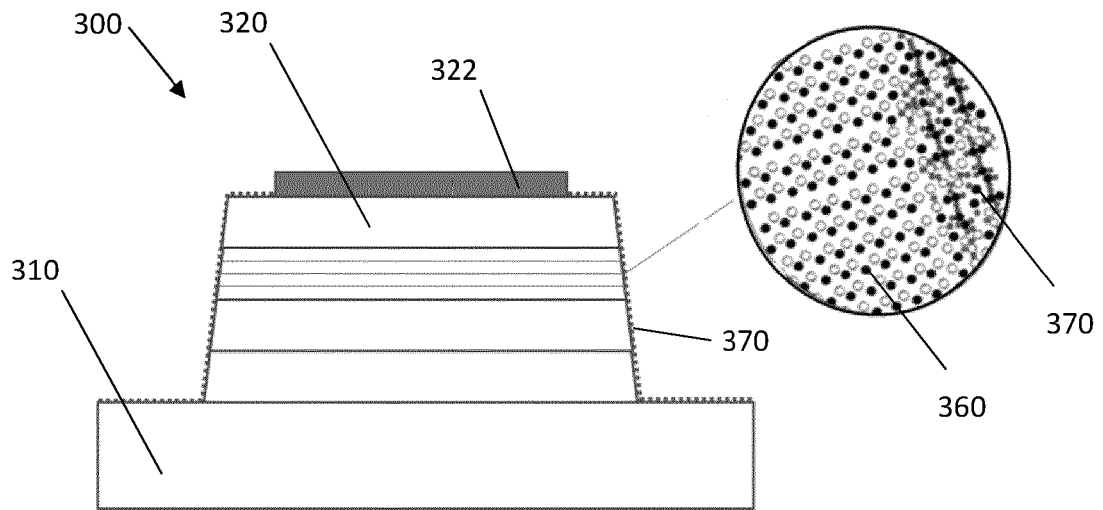


Fig. 3A

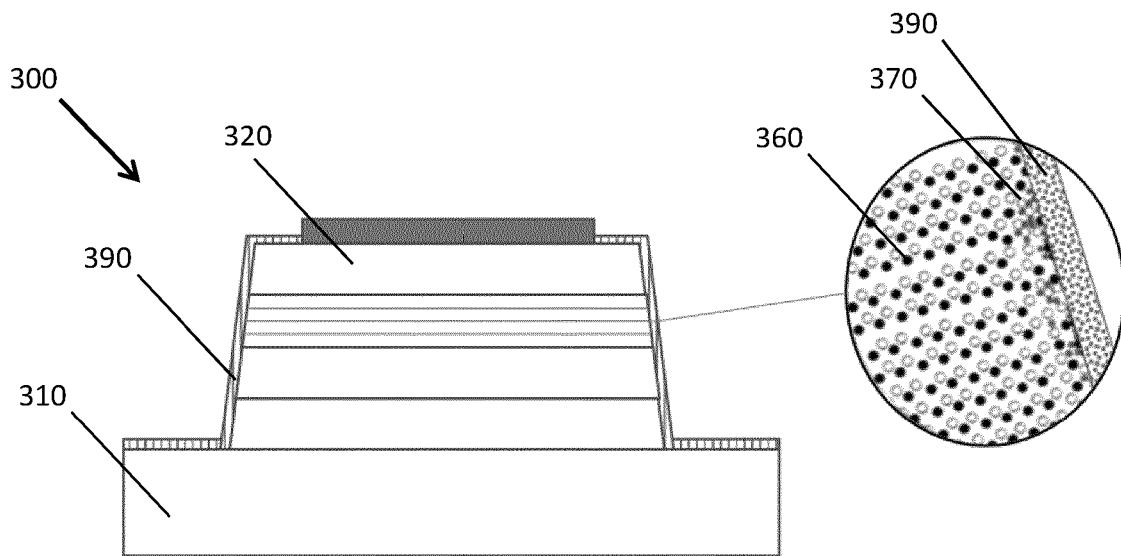


Fig. 3B

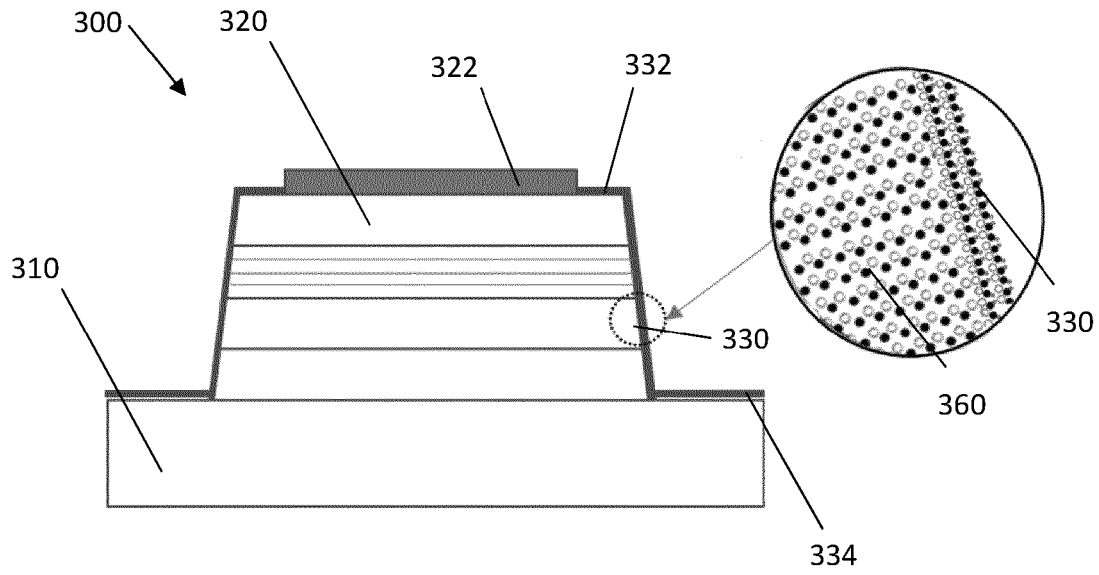


Fig. 3C

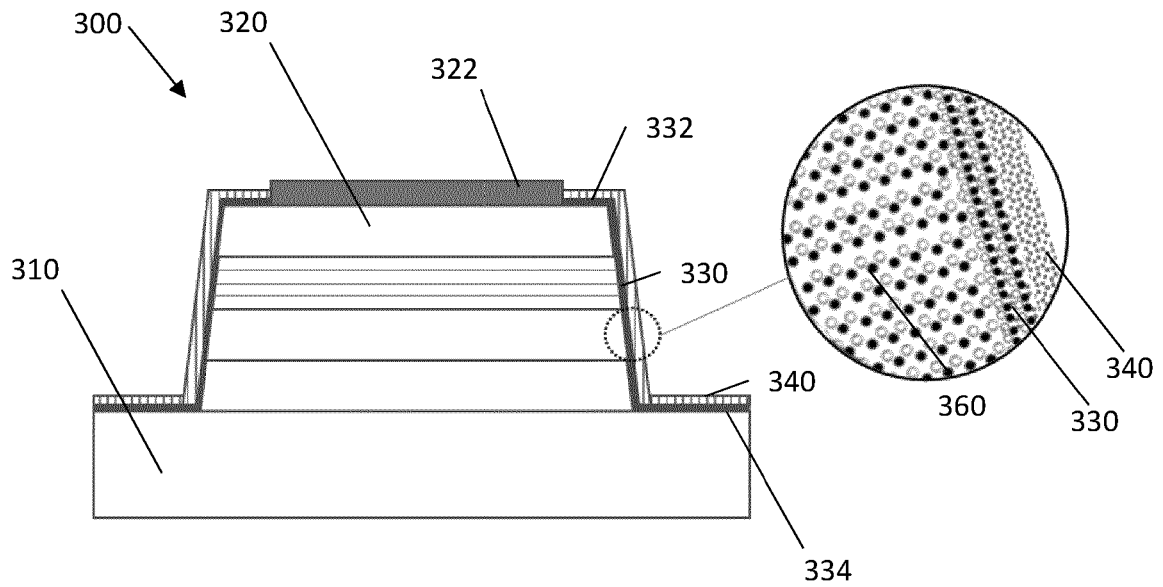


Fig. 3D

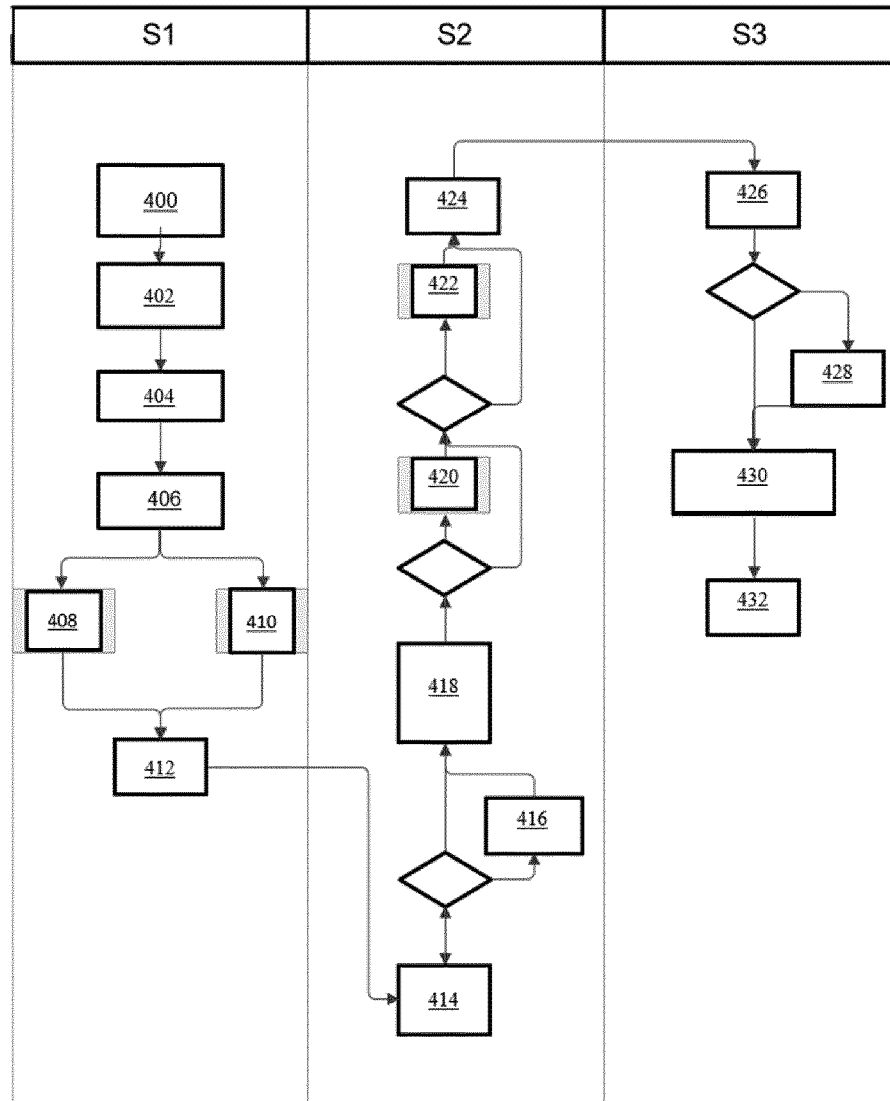


Fig. 4

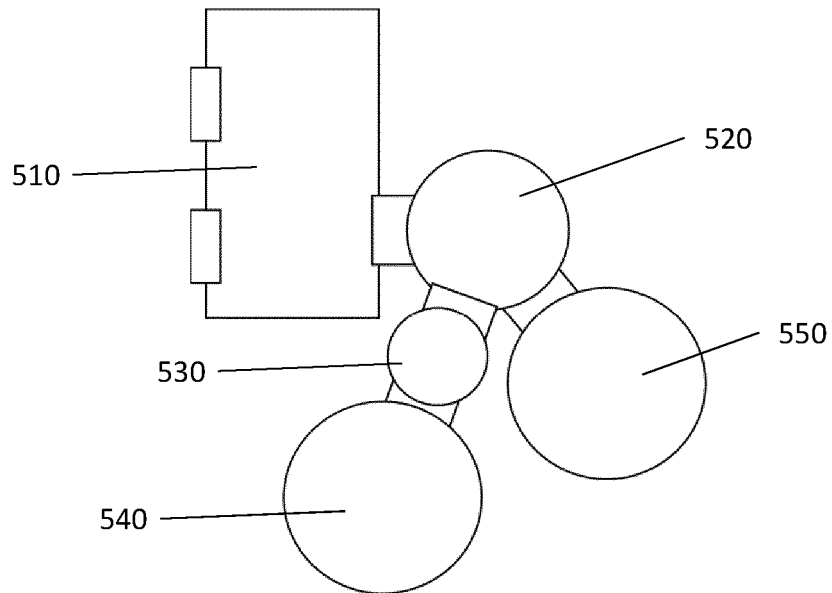


Fig. 5

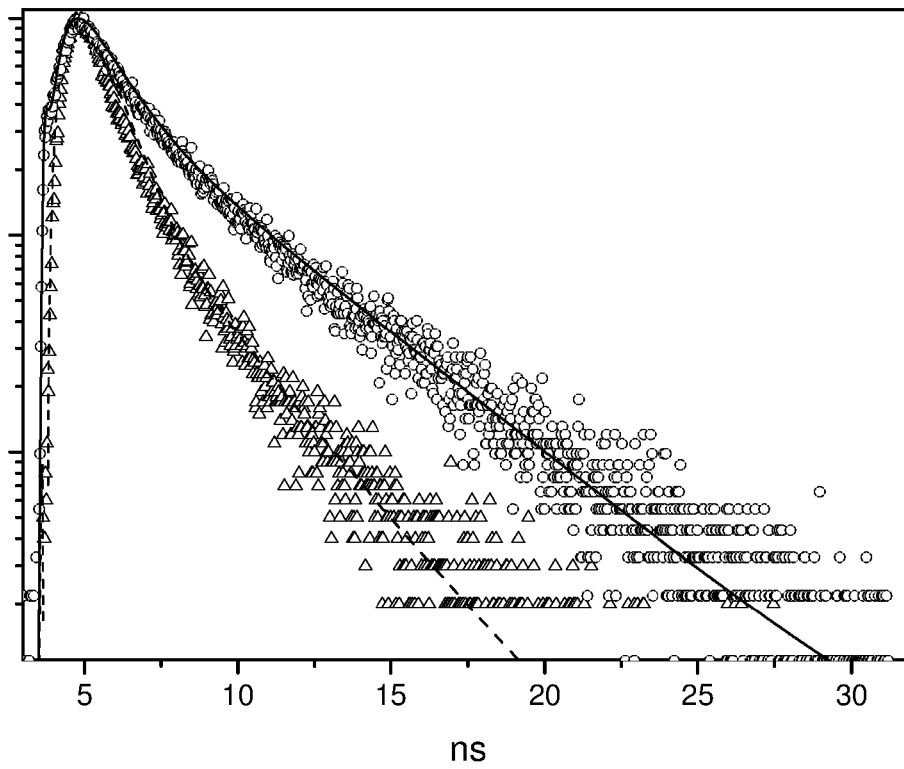


Fig. 6

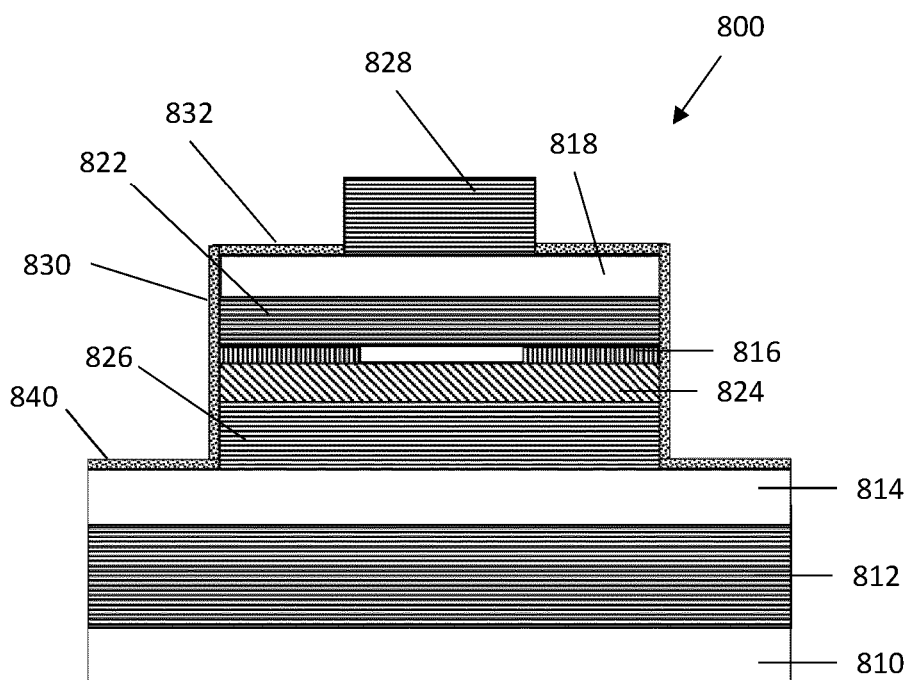
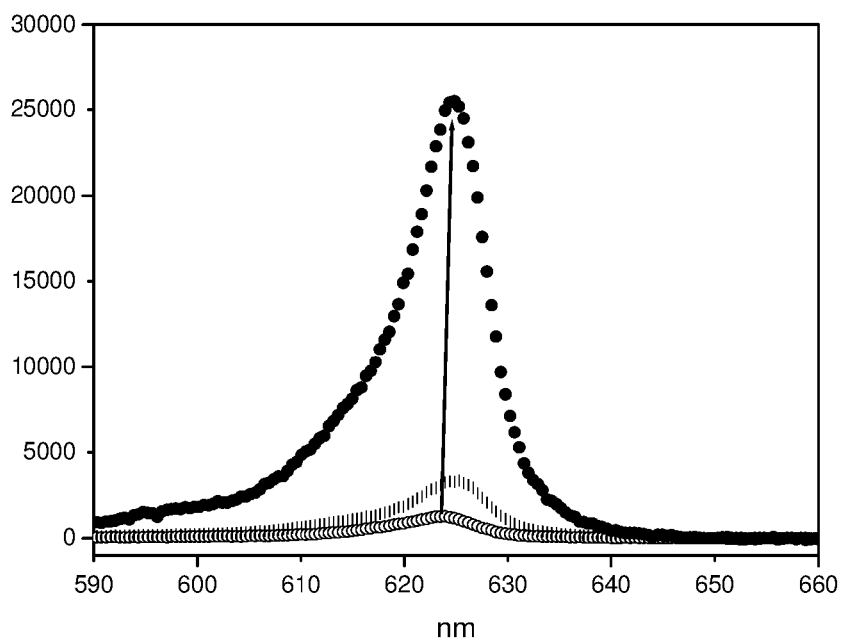


Fig. 8

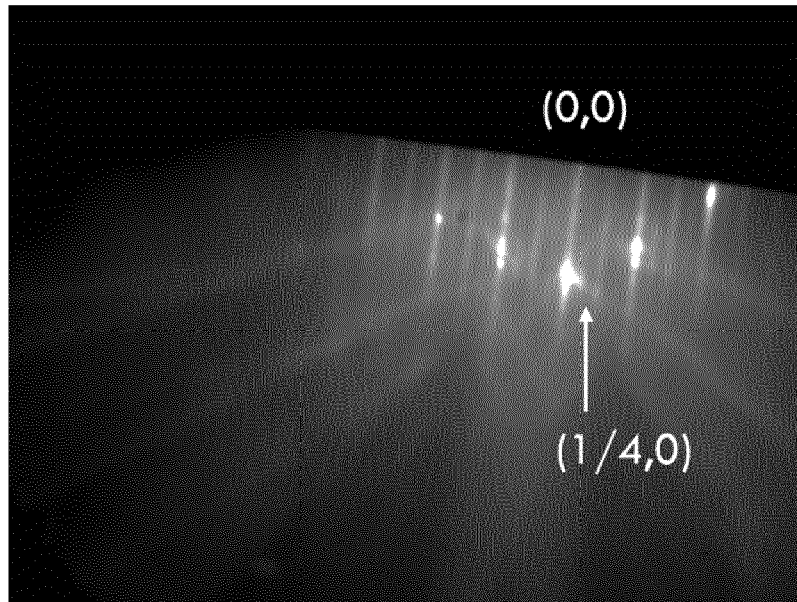


Fig. 9A

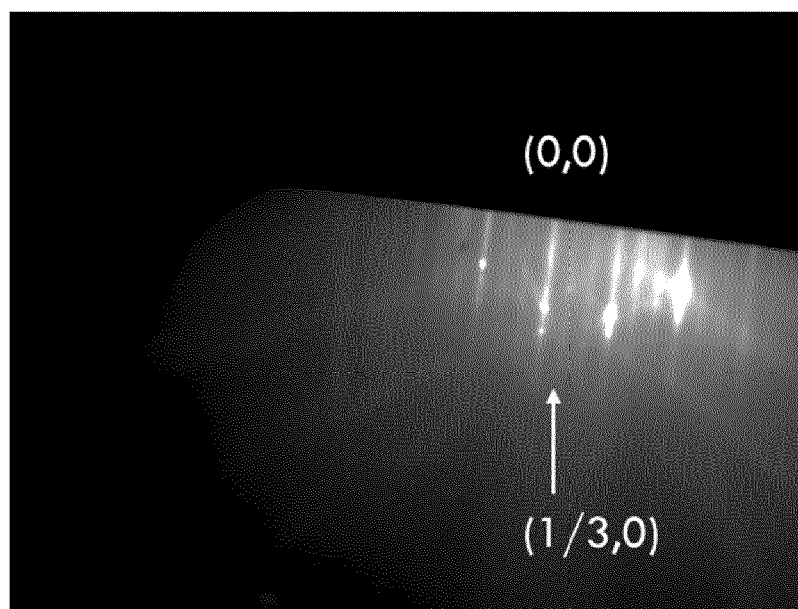


Fig. 9B

9/11

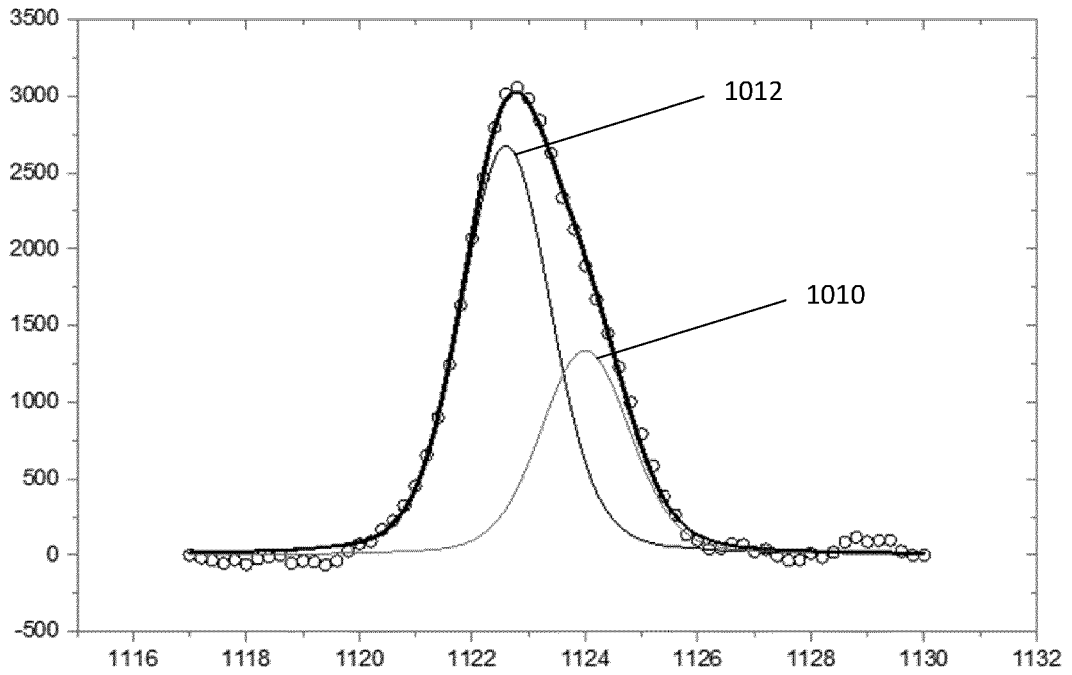


Fig. 10A

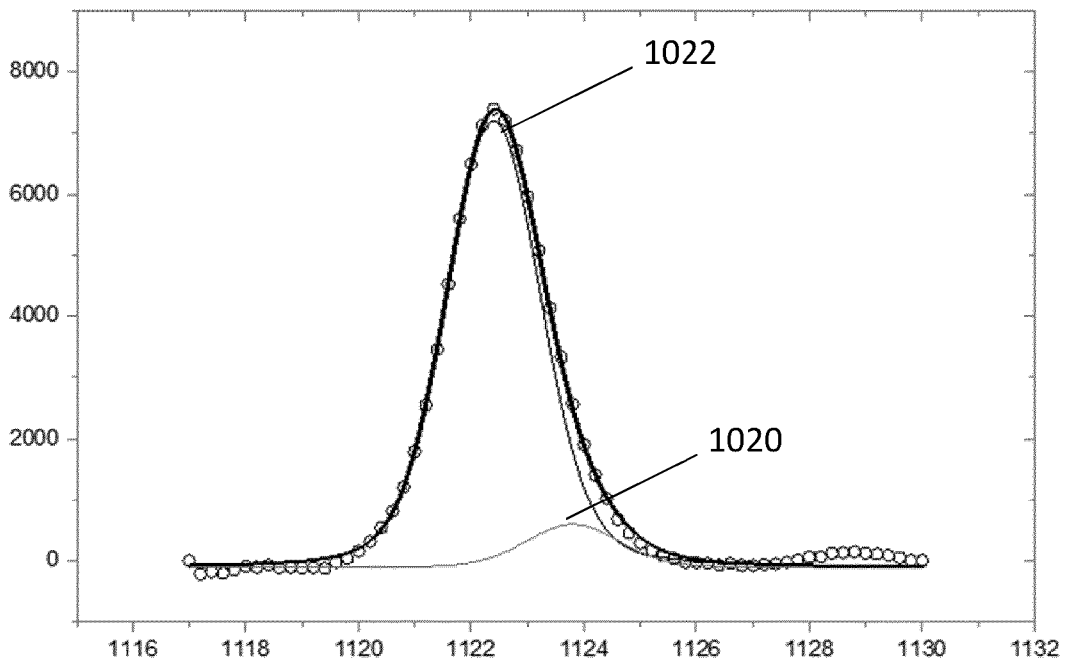


Fig. 10B

10/11

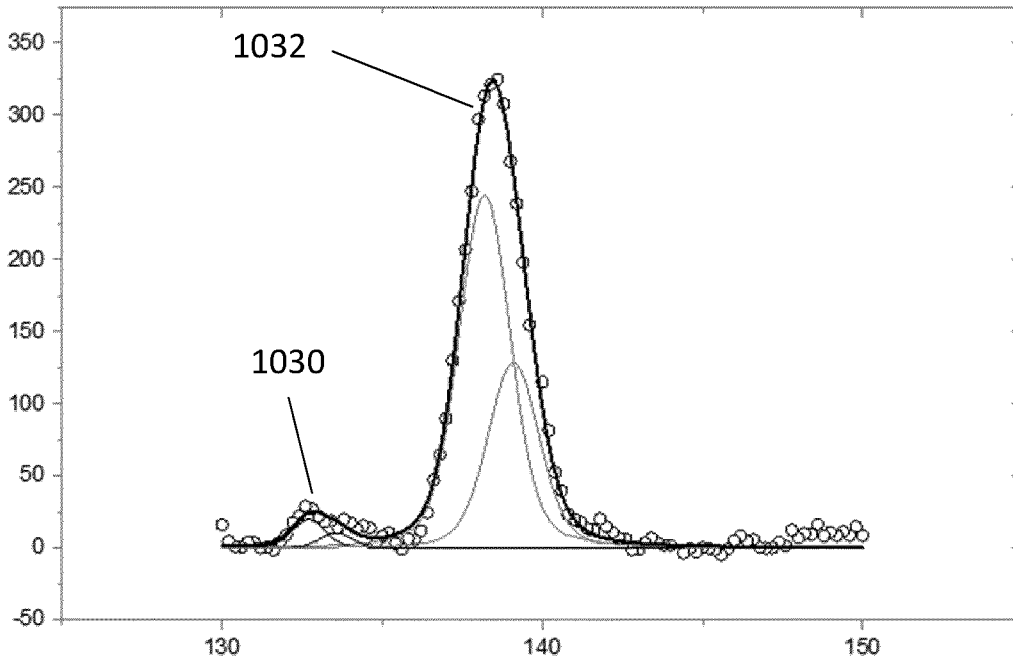


Fig. 10C

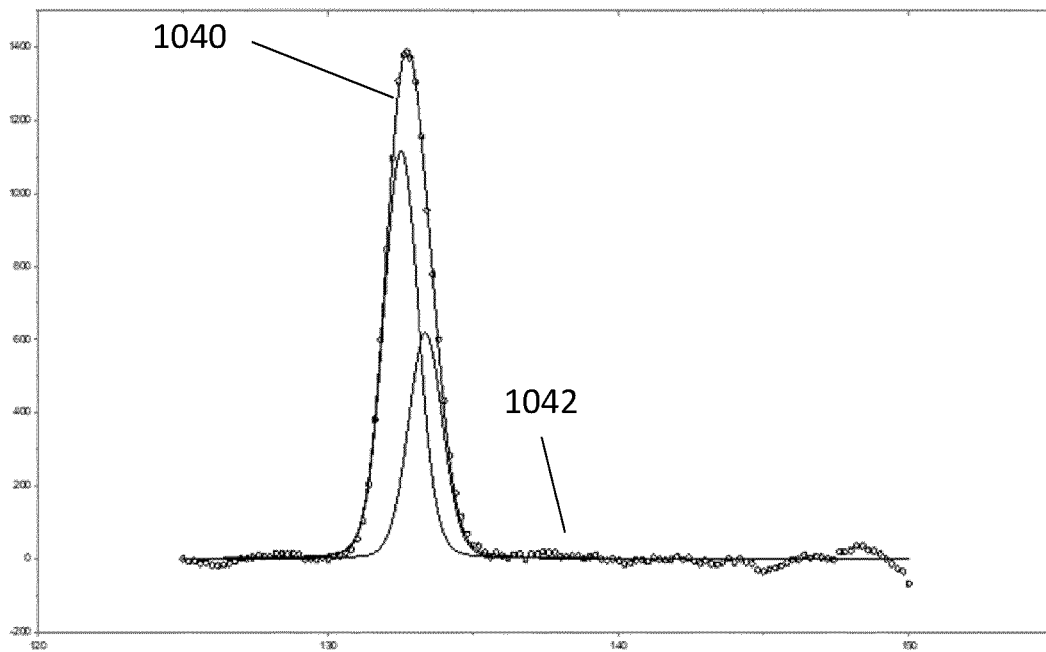


Fig. 10D

