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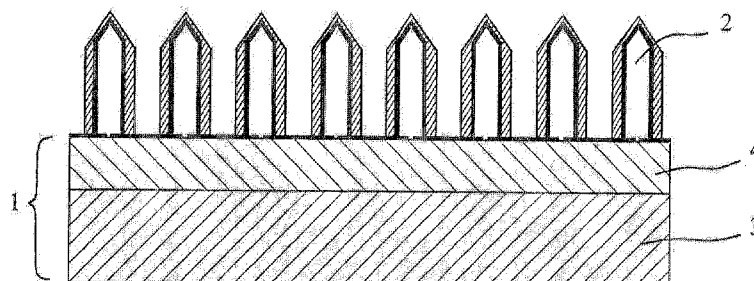


Fig. 1

(57) Abstract: The present invention provides a substrate (1) with a bulk layer (3) and a buffer layer (4) having a thickness of less than 2  $\mu\text{m}$  arranged on the bulk layer (3) for growth of a multitude of nanowires (2) oriented in the same direction on a surface (5) of the buffer layer (4). A nanowire structure, a nanowire light emitting diode comprising the substrate (1) and a production method for fabricating the nanowire structure is also provided. The production method utilizes non-epitaxial methods for forming the buffer layer (4).

## SUBSTRATE WITH BUFFER LAYER FOR ORIENTED NANOWIRE GROWTH

Technical field of the invention

The present invention relates to nanowire based devices and in particular to substrates for nanowire growth.

5 Background of the invention

In nanowire based devices, such as nanowire based light emitting diodes (LEDs), a multitude of nanowire based structures are usually arranged in ordered arrays on a substrate. The substrate often has multiple purposes, i.e. being a template for nanowire growth, being a carrier for the nanowires in the device and electrically connecting the nanowires on one side thereof. Different techniques for growth of the ordered arrays of nanowire based structures, where all structures are parallel and oriented in the same direction, are known. For example, semiconductor nanowires may be epitaxially grown on a high quality, mono-crystalline, semiconductor layer of the substrate, typically by selective area growth with a patterned growth mask arranged on the substrate, as described in e.g. WO 2007/102781. Another common method is the so called VLS (vapour-liquid-solid) technique where a pattern of catalytic particles, often Au, is used as seeds to grow the nanowires, as described in US 7,335,908.

20 Nitride semiconductors, such as GaN, InN and AlN and their GaInN, GaAlN, and GaInAlN combinations of various composition are of used in blue, green and UV LEDs and other optoelectronic applications due to their wide and direct bandgap. Typically these devices nitride semiconductors are grown in planar layers on a substrate. However, mismatch between substrate and the nitride semiconductors, for example lattice mismatch, introduce detrimental defects cracks in the grown material. In prior art dislocations has been suppressed by using epitaxial substrates or substrates with an epitaxial buffer layer. Commercial GaN based devices utilizes sapphire, Si or SiC substrates, which, are highly lattice mismatched to GaN, and hence several  $\mu\text{m}$  thick buffer layers are epitaxially grown on the substrates in order to function as a strain accommodating layers and a high quality epitaxial foundation to grow the device on. Examples of the use of epitaxial buffer layers can be found in the following documents.

30 Us 6,523,188 B2 discloses epitaxial growth of an epitaxial buffer layer made of AlN on a Si (111) substrate before growing the GaN layer to compensate for the

large lattice mismatch between GaN and Si. The epitaxial buffer layer is preferably less than 0.2 $\mu$ m in order to obtain a flat GaN layer.

In US 6,818,061 B2 discloses epitaxial growth of a thin epitaxial buffer layer including AlN with a thickness of about 40nm on a Si (111) substrate before  
5 growing the GaN layer to compensate for the large lattice mismatch between GaN and Si. Moreover, the GaN layer includes interlayers with alternating AlN and GaN layers.

In US 6,617,060 B2 it is disclosed that a compositionally graded transition layer made of a GaN alloy between a Si substrate and a GaN layer, and optionally  
10 additionally a thin epitaxial strain accommodating layer that generally has a constant composition throughout its thickness, can be used to prevent crack formation in the GaN layer. Without this compositionally graded transition layer cracks can not readily be prevented.

US 7,365,374 B2 discloses the use of a strain absorbing layer on a substrate.  
15 The strain absorbing layer should have a thickness of less than 10 nm so that overlying layers have an epitaxial relation ship with the underlying substrate.

It is appreciated from the above examples that in prior art methods the buffer layer is grown by epitaxial growth methods in order to form thick single  
crystalline, high quality, epitaxial buffer layers. Together with the GaN device layer  
20 grown on the epitaxial buffer layer an epitaxial layer with a thickness of more than 3 $\mu$ m is formed.

Recently the use of nitride semiconductors for nanowire based devices has received considerable attention since the nanowires enable growth of nitride semiconductor materials with low defect density, as described in WO  
25 2008/085129 A1. However, even if nanowires are used, the growth of high-quality nitride semiconductors, for example GaN, is performed using high-quality epitaxial layers as templates. The use of epitaxial layers of high quality ensures an optimal epitaxial template for nanowire growth, minimizes the density of defects that may continue up in the nanowires, and enables low electrical resistance  
30 between the substrate and nanowires. However, a buffer layer in accordance with prior art introduces substrate bowing due to the strain, which radically alters the thermal profile over the substrate. For nanowire growth, high thermal uniformity on the substrate during growth is crucial for fabrication of nanowire structures such as LEDs. The problem of substrate bowing is enhanced by increasing size of  
35 the substrate, in this way being an obstacle for large-scale processing of GaN

devices on large substrates. Growth of the buffer layer is a time consuming procedure and often thick AlN is used in the buffer layer, which limits the vertical conductivity. Moreover, for many optoelectronic devices, for example LEDs the substrate is often removed, leaving only the buffer layer in the final device,

5 whereby the costly substrate material only is used for the growth step.

In LEDs, reflectors may be used under the light emitting region to direct light out from the LED. Most common is the use of metal reflectors, as Ag mirrors.

Bragg reflectors comprise repeated epitaxial semiconductor layers with different refraction index forming a. Bragg reflectors are limited in their reflectivity over a

10 narrow span of wavelength and incident light angle and are not suitable for devices emitting light in a wider wavelength region.. The narrow optimal

wavelength window is less of a problem as LEDs do emit light of narrow

wavelength. However, , growth of Bragg reflectors is time consuming, and

particularly challenging on lattice mismatched substrates, since the crystal

15 quality has to be high to make efficient reflectors.

#### Summary of the invention

In view of the foregoing one object of the invention is provide substrates for growing a multitude of nanowires oriented in the same direction, which substrates do not require costly and time consuming epitaxy and enable use of different

20 substrate materials than used today. In particular one object of the invention is to allow use of materials formed with higher defect and dislocation density than commonly obtained with epitaxial growth techniques.

The objects of the invention are achieved by the substrate and the method as defined in the independent claims.

25 A substrate in accordance with the invention comprises a bulk layer and a buffer layer arranged on the bulk layer for growth of a multitude of nanowires oriented in the same direction on a surface of the buffer layer. The thickness of the buffer layer that is deposited on the substrate is preferably less than 2 $\mu$ m. In prior art buffer layers of substrates for growing nanowires the strain compensating

30 buffer layer thickness is in the range of 3-10 $\mu$ m, and grown using epitaxy in order to provide as high crystal quality to the buffer layer as possible..

The substrate can be used to form a structure comprising one or more nanowire based structures protruding from the buffer layer. This structure can be a nanowire based light emitting diode structure where the nanowire based

35 structures are utilised for light generation.

A method according to the invention for forming a structure comprises a multitude of nanowires oriented in the same direction in accordance with the invention comprises the basic steps of: providing a bulk layer; depositing a buffer layer with a thickness of less than  $2\mu\text{m}$  on the bulk layer; and growing one or  
5 more nanowires on the buffer layer.

The invention includes, but is not limited to sub- $\mu\text{m}$  thickness nitride, oxygen and carbon containing buffer layers on substrates such as sapphire, quartz and Si. The buffer layers may include a reflector part and they may be laterally conducting in order to be integrated electronically with the nanowire devices.

10 The invention furthermore teaches how to fabricate large area wafers with heavily reduced bow, as compared to previous buffer layers for nanowires. Here expressed in curvature, with measured wafer curvature less than  $50\text{ km}^{-1}$ , preferably less than  $40\text{ km}^{-1}$ , in some embodiments the curvature is less than  $30\text{ km}^{-1}$  preferably less than  $20\text{ km}^{-1}$ .

15 The inherent one-dimensional nature of nanowires makes it rational to argue that growth of nanowires should be possible on other substrate materials or substrates of lower quality. While this may not have been proven yet, it has, for example in WO 2004/004927 A2, been shown that nanowires have a much higher capacity to adapt for highly lattice mismatched axial variations without  
20 introducing crystal defects than structures of the same composition grown in planar mode. Thanks to the invention it is possible to use buffer layers that have lower crystalline quality and even polycrystalline buffer layers.

Properties of the buffer layer can be divided into device enhancing properties and growth enabling properties. Depending on end use and final configuration of  
25 the device parameters as, thermal conductivity, CTE, transparency, refraction index, absorption and electrical conductivity are of importance. The growth enabling properties are thermal resistance to the used growth temperature, the capacity of the substrate to provide a generic direction to multiple nanowires, strain induced bowing of the substrate and the possibility to nucleate the NW material on the  
30 substrate. Nitride based III-V semiconductors have been shown to be possible to nucleate on many materials comprising N, O, or C. However, the nucleation step in itself cannot always be made in an oriented-constrained manner, so usually it is convenient to keep this step as short as possible.

Traditionally, buffer layers for planar and selectively grown nitride based  
35 semiconductor devices, of devices have been, thick, epitaxially grown, often in

multiple steps, comprising multiple III-N materials, all to increase device performance. Device quality has been directly dependent of crystalline quality of the substrate. Then substrate material choices have also been limited to the use of high crystalline materials of SiC, Si and Al<sub>2</sub>O<sub>3</sub> with choice of substrate directly  
5 determining buffer layer quality and therefor device quality.

One advantage with the buffer layer in the substrate of the invention is that material choices and material sequences of the substrates are appreciably relaxed, creating new options to electrically integrate the substrate with the nanowire  
10 array and enabling the use of non-Bragg reflectors or multi-wavelength Bragg reflectors in the substrate.

By being able to use partly crystalline buffers with partly directional properties only, the possible choices of substrate material have been further increased, where buffer layer materials that do not even need directional information from the  
15 substrate are used, such as AlN, some Carbon films, TiN and similar.

While using our proprietary nanowire fabrication method described herein as described for example in U.S. Patent Number 7,829,443, to Seifert et al., incorporated herein by reference for the teaching of nanowire fabrication methods, we have found that we can lessen the above described constraints to the buffer layer  
20 and therefore also the substrate. This may be possible to achieve with other nanowire growth methods although this has not been investigated by us.

A full understanding of the mechanisms enabling this invention is not yet achieved. However, the unique directionality of the NW growth in combination with the small width of the nanowires, giving the crystal the option to deflect or redirect  
25 defects at an early stage of growth is understood to play major roles. Energy minimization of the crystal is achieved with increased crystal perfection. The possibilities for the crystal to relax in all directions during growth together with the proximity of surfaces to consume dislocations are understood to be of importance.

Another advantage with the invention is that no thick strain compensating  
30 buffer layer has to be used for the nanowire growth. With a thick strain compensating buffer layer the processing often suffers from bowing of the substrate, which may crack the substrate or at least introduce non-uniform growth conditions over the substrate that deteriorate the performance of the final device.

It is a further advantage of the invention that it makes it possible to grow oriented nanowires on cheaper substrates, such as Si (111) substrates, and in particular Si (100) substrates, but also amorphous substrates, the main prerequisite being the substrate being able to resist the chosen process

5 temperatures.

Another advantage of the invention is to provide substrates for growing nanowires that can remain in the final device. For example, as mentioned above, in LED structures the substrate is usually removed since it cannot be used in the device, or due to insufficient thermal properties. With for example Si substrates

10 the substrate can remain and be used.

Yet another advantage with the invention is that costly and time consuming epitaxy steps in the processing are avoided.

Thanks to the substrate for growing nanowires and the method for growing nanowires of the invention, the next step in development of nitride based semiconductor devices, and in particular GaN-based devices, such as LEDs, will

15 be possible.

Thus, in one aspect the invention provides a nanowire LED structure, wherein each nanowire in use contributes to the formation of an active region for generation of light.

20 Embodiments of the invention are defined in the dependent claims. Other objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings and claims.

25 Brief description of the drawings

Preferred embodiments of the invention will now be described with reference to the accompanying drawings, wherein

FIG. 1 schematically illustrates a nanowire structure with a substrate in accordance with prior art,

30 FIG. 2 schematically illustrates a nanowire structure with a substrate in accordance with the invention,

FIG 3 schematically illustrates a nanowire structure comprising a multilayer structure in the buffer layer in accordance with the invention,

FIG. 4 shows a nanowire array of GaN nanowires formed on a low quality buffer layer on a Si substrate in accordance with the invention, FIG. 5 shows a low quality buffer layer in accordance with the invention, and FIG. 6 illustrates schematically a nanostructure comprising a core and a shell.

## 5 Detailed description of embodiments

All references to vertical, lateral etc. are introduced for the ease of understanding only, and should not be considered as limiting to specific orientation. Furthermore, the dimensions of the structures in the drawings are not necessarily to scale.

10 Although the preferred embodiment of the invention in the following are described mainly in terms of nanowire light emitting diodes (LEDs) and the needs for such structures it should be appreciated that the substrates and buffer layers of the invention and the nanowire growth thereon can be used to fabricate other optoelectronic devices and electronic devices and to fulfill the needs thereof.

15 For LEDs nitride-based semiconductor materials are of great interest at least for the part of the device that generates the light. Typical GaN nanowire LED fabrication includes elevated growth temperatures around 1000 deg C. Substrate/buffer layer materials must be chosen according to this thermal envelope. Examples of such materials are Al<sub>2</sub>O<sub>3</sub> (isolator), AlN, GaN, Si, (semiconductors), and W (metals). Extra  
20 precautions have to be taken with adjacent combinations of layers that may form a eutectic binary compound with a melting point much lower than 1000 degrees C. Intermediate layer combinations may then be used as barrier layers. Since the skilled person is familiar with these risks these barrier layers are not explicitly disclosed in the embodiments.

25 FIG. 1 schematically illustrates a prior art nanowire based structure comprising a substrate 1 with a bulk layer 3 having a thickness in the range of 20-1000µm and an epitaxial strain accommodating buffer layer 4 having a thickness in the range of 3-10µm. Nanowires 2 protrude from the buffer layer 4. The nanowires 2 are aligned in one direction which is determined by the crystal orientation of the buffer layer 4.

30 FIG. 2 schematically illustrates a structure in accordance with the invention comprising a substrate 1 with a bulk layer 3 having a thickness in the range of 20-1000µm and an epitaxial strain accommodating buffer layer 4 having a thickness of preferably less than 2µm, more preferably in the range of 0.2-2µm. Nanowires 2



protrude from the buffer layer 4. The nanowires 2 are aligned in one direction which is determined by the orientation of the buffer layer 4.

The general crystal structure of the buffer layer is often the same or at least similar to the nanowire crystal structure. It is however the atomic configuration of the buffer layer structure that in the end forces the nanowires to grow unidirectionally. Alteration of preferred general alignment of nanowires can be realized with process steps, as explained in the following. In such cases the orientation of the nanowire crystal is usually adapted to the buffer layer crystal orientation.

By way of example, in the structure in FIG. 2 the nanowire based structures comprise a radial core-shell structure forming a nanowire based LED structure. The core-shell structure may comprise an n-type GaN nanowire core and a p-type GaN shell with an intermediate quantum well layer comprising sub-layers of AlGaIn, InGaIn and/or GaIn. FIG. 2 illustrates nanowires grown using selective area growth using a growth mask, however not limited to this.

Fig. 3 schematically illustrates one embodiment of the invention comprising a buffer layer 4 with one or more sub-layers 4a, 4b, 4c. The buffer layer 4 or said one or more sub-layers 4a, 4b, 4c may comprise semiconductor materials, metal/metal alloys and/or insulators in different layers. Non-epitaxial materials with orientational properties that improve thermal properties of the device, can withstand the growth temperatures are preferred, exemplified, but not limited to AlN, TiN, graphene, and other polycrystalline or partly amorphous carbon films.

In one embodiment of the invention the buffer layer or each of the sub-layers has a homogeneous composition throughout its thickness. At least the composition is not intentionally varied.

Different materials can be combined to obtain desired optical and/or electrical properties. For example one or more reflector layers may be included in the sub-layer stack of the buffer layer 4. The electrical conductivity in vertical and lateral direction can also be tailored, for example in order to have a high conductivity in the lateral direction to provide a current spreading layer connecting the nanowires of the structure.

The nanowire structures are electrically connected by a common lateral contact formed by the buffer layer 4 or at least one of said one or more sub-layers 4a, 4b, 4c.

5 There are several deposition methods available that may be used for formation of the buffer layer 4 or the sub-layers 4a, 4b, 4c when low defect densities and high crystal perfection are not needed. Different deposition methods may be used for different sub-layers.

Buffer layers deposited by atomic layer deposition (ALD) have excellent orientation properties.

10 Plasma- enhanced chemical vapor deposition (PECVD), low pressure chemical vapor deposition (LPCVD) and atmospheric pressure chemical vapor deposition (APCVD) can be used. For example, oriented AlN can be grown with LPCVD and APCVD, graphene, and other polycrystalline or partly amorphous carbon films can also be deposited by utilizing LPCVD or RF-CVD. Generally PECVD has inferior  
15 orientation capacity as compared with the other two.

Physical vapor deposition techniques based on sputtering or evaporation can also be used, however sputtering is usually not feasible for oriented deposition. Vacuum evaporation methods are often preferred for oriented deposition of metals or metal alloys. A good example is aluminum layers that easily are  
20 grown/evaporated with uniform (111) orientation perpendicular to the substrate although it usually is polycrystalline with high variation of grain size. However, the low melting point at 660 deg C limits the used of aluminum.

Lattice mismatched layers can also be grown with epitaxial methods. Epitaxy methods such as metal organic chemical vapor deposition (MOCVD) or hydride  
25 vapour phase epitaxy (HVPE) are usually used to fabricate crystals and crystal interfaces of very high perfection. However, when used for growth on lattice mismatched substrates, the dislocation densities of the layers are high. The buffer layer 4 or one or more of the sub-layers 4a, 4b, 4c can have a defect or dislocation density higher than  $10^{-10}/\text{cm}^2$  and still be used for commercial devices.

30 Layer quality can be increased to a certain extent by growing thick strain accommodating buffer layers, often at low temperature. Without the constraint of crystal perfection thick strain accommodating buffer layers are made redundant.

Oxidation of oriented buffer layers can preserve the orientation of the original substrate. An illustrating example is evaporated aluminum that can be oxidized to  $\text{Al}_2\text{O}_3$  with preserved orientation. However, deposition of a buffer layer can also alter the orientation.

5 A method for forming a structure comprising a multitude of nanowire structures oriented in the same direction, wherein the method comprises the steps of:

- providing a bulk layer 3;
- depositing a buffer layer 4 with a thickness of less than  $2\mu\text{m}$  on the bulk layer 3;

10 and

- growing one or more nanowires 2 on the buffer layer 4.

The method of the invention enables the fabrication of both Bragg reflectors and normal reflector layers. Bragg reflectors made by deposition, i.e. not epitaxy, are easier and cheaper to fabricate than epitaxial Bragg reflectors. This method is  
15 therefore suitable for fabrication of multi colored devices, using multiple, stacked Bragg reflectors, formed by a plurality of sub-layer, each Bragg reflector reflecting a separate light emitting wavelength, used in conjunction with colored light emitting sources on top of the substrate. However, each Bragg reflector, adds approximately  $0.5\mu\text{m}$  to the thickness of the buffer layer, making the buffer layer thicker than in  
20 single colored devices.

The deposition methods are exemplified above. In principle there are two types of deposition in accordance with the invention: (i) preservation of orientation of bulk layer; and (ii) creation of an oriented buffer layer for growth of nanowires with predetermined crystal orientation on bulk layers, i.e. commonly denoted substrates,  
25 without preferential orientation or with different orientation.

In the first type (i) semiconductor nanowires are commonly grown in the (111) (cubic zinc blende) or (0001) (hexagonal wurtzite) direction. For oriented growth of nanowire arrays a (111) or (0001) substrate is usually used, so that the nanowires will be oriented perpendicularly to the substrate surface. Controlled deposition of  
30 materials on crystalline substrates with respect to orientation will facilitate preserving the orientation, which facilitates orientated growth on multi-layered structures.

In the second type (ii), for some materials and deposition methods, such as AlN fabricated with LPCVD or APCVD, or vacuum evaporated Al, the material layers

themselves tend to align in a predominant (111) direction. This is also true for TiN, where many large area deposition methods are available. The use of such materials increases the freedom of choice for the underlying layers as the directional information can be introduced in the last layers, which is designated for nanowire nucleation

Although nanowires may be nucleated on a variety of materials, homogeneous nucleation is greatly facilitated by growing them on similar material substrates. For nitride based structures, such as GaN nanowires, optimal substrate surfaces for growth are nitride based semiconductors such as GaN, InN or AlN and combinations thereof. AlN, but also TiN, also allows adjacent sub-layers of SiO<sub>2</sub>, TiO<sub>2</sub> or SiN<sub>x</sub>. Preferential termination layers AlN or a sequence of GaN and AlN can easily be grown with ALD, CVD and MOCVD methods. In this case the AlN or TiN can be used to enhance directional information while addition of Ga into the terminating surface layer will enhance nucleation homogeneity.

By depositing a layer of grapheme, polycrystalline carbon or partly amorphous carbon, using for example LPCVD, for growing nanowires a growth direction perpendicular to the substrate can be obtained. The reason for this is the crystallographic properties of high temperature resistant carbon films i.e., providing grains of diamond-like or graphene like material. A special nucleation step and nucleation temperature is often required in order to initiate growth of ionic material such as GaN on materials such as Si or C. However, the nucleation step will often lessen the directional constraint to the growth conditions and should usually be kept short. The grain structure may help to relax lattice strain between the nanowire and the film although a "too random" grain structure will limit directional properties and temperature resistance of the film. Further advantages of using carbon films in the buffer layer or in one or more sub-layers of the buffer layer are their excellent heat conducting properties as well as their inherent transparency.

WO 2008/085129 relates to nitride nanowires and method of producing such. The methods of that application can be implemented for growth on buffer layers in accordance with the present invention. In particular, nitride based semiconductor nanowires can be accomplished on a buffer layer in accordance with the invention by a selective area growth technique wherein the nitrogen source flow rate is substantially constant during nanowire formation. By altering the III/V-ratio during growth a shell layer that at least partly encloses the nanowire can be obtained.

Thanks to the invention it is possible to use the method of WO 2008/085129 to

grow nanowires on cheaper substrates, such as Si substrates, and with buffer layers that are not single crystalline or with extremely low levels of defects.

FIG. 4 shows a nanowire array of GaN nanowires formed on a low quality buffer layer on a Si substrate in accordance with the invention.

5 FIG. 5 shows a low quality buffer layer in accordance with the invention.

In one embodiment of the invention a selective area growth technique utilizing holes in a mask layer arranged on the buffer layer in accordance with the invention functioning as apertures for nanowire growth is used. The selection of hole diameter is important for obtaining single crystalline, dislocation free nanowires. If the hole  
10 diameter is too large the nanowires may be too wide to be able to repel dislocations, or may not be single crystalline. The critical hole diameter depends on the buffer layer quality and composition as well as the composition of the nanowire and conditions during nanowire nucleation and growth, but generally the hole diameter is preferably less than 200nm, more preferably less than 150nm. In embodiments of  
15 the invention the hole diameter is also preferably less than 100nm, more preferably less than 50nm.

Although the fabrication method described herein preferably utilizes a nanowire core to grow semiconductor shell layers on the cores to form a core-shell nanowire based structure forming a LED, as described for example in U.S. Patent  
20 Number 7,829,443, to Seifert et al., incorporated herein by reference for the teaching of nanowire fabrication methods, it should be noted that the invention is not so limited. For example, as will be described below, in the alternative embodiments, only the core may constitute the nanostructure (e.g. nanowire) while the shell may optionally have dimensions which are larger than typical  
25 nanowire shells. Furthermore, the device can be shaped to include many facets, and the area ratio between different types of facets may be controlled. This is exemplified in FIG. 6 by the "pyramid" facets and the vertical sidewall facets. FIG. 6a shows a pillar shaped nanostructure 60 comprising a nanowire core 62 and a shell 64, and FIG. 6b shows another variant where the shell is grown on a  
30 nanowire core 62 so as to form a pyramid 66. It should be noted that FIG. 6 is only a schematic illustration, and is not to scale, and the shell while shown as a single layer could comprises several layers. The LEDs can be fabricated so that the emission layer formed on templates with dominant pyramid facets or sidewall

facets. The same is true for the contact layer, independent of the shape of the emission layer.

The use of sequential (e.g., shell) layers gives that the final individual device (e.g., a pn or pin device) may have a shape anywhere between a pyramid shape (i.e., narrower at the top or tip and wider at the base) and pillar shaped (e.g., about the same width at the tip and base) with circular or hexagonal or other polygonal cross section perpendicular to the long axis of the device. Thus, the individual devices with the completed shells may have various sizes. For example, the sizes may vary, with base widths ranging from 100 nm to several (e.g., 5)  $\mu\text{m}$ , such as 100 nm to below 1 micron, and heights ranging from a few 100 nm to several (e.g., 10)  $\mu\text{m}$ .

With the methods according to the invention it is possible to make large area wafers with heavily reduced bow, as compared to previous buffer layers for nanowires. The bow is herein expressed as curvature, with measured wafer curvature less than  $50 \text{ km}^{-1}$ , preferably less than  $40 \text{ km}^{-1}$ , in some embodiments the curvature is less than  $30 \text{ km}^{-1}$  preferably less than  $20 \text{ km}^{-1}$ . Curvature as used herein is defined in an article by E. Armour et al., "LED growth compatibility between 4" and 6" sapphire" in "Semiconductor TODAY Compounds & advanced Silicon", Vol. 4, Issue 3, April/May 2009, p 82-86, the article being incorporated herein in its entirety by reference (see Figure 4 therein).

Thus, Bow (B) and Curvature (K) are related as follows:

$$K = 1/R$$

$$B = K * D^2/8$$

wherein

R is the radius of the curvature of the wafer, and

D is the diameter of the substrate (e.g. 2, 4 or 6 inches)

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, on the contrary, it is intended to cover various modifications and equivalent arrangements within the scope of the appended claims.

## CLAIMS

1. A substrate (1) with a bulk layer (3) and a buffer layer (4) arranged on the bulk layer (3) for growth of a multitude of nanowires (2) oriented in one and the same direction on a surface (5) of the buffer layer (4), wherein the buffer layer (4) has a thickness of less than  $2\mu\text{m}$ .
2. The substrate (1) of claim 1, wherein the buffer layer (4) has a thickness of 0.2- $2\mu\text{m}$ .
3. The substrate (1) of claim 1 or 2, wherein the buffer layer (4) comprises a plurality of sub-layers (4a, 4b, 4c).
4. The substrate (1) of any of claims 1-3, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are made of a semiconductor material.
5. The substrate (1) of claim 4, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) comprise a nitride-based III-V semiconductor material.
6. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are made of a metal or metal alloy.
7. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are made of an insulator.
8. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are made of graphene.
9. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are made of TiN.
10. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) and one or more of the sub-layers each are deposited using a deposition technique selected from the group of: LPCVD, APCVD, PECVD, ALD, PVD, MOVPE, or HVPE.
11. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) function as a reflector for radiated light.
12. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) has a defect or dislocation density higher than  $10^{-10}/\text{cm}^2$ .

13. The substrate (1) of any of the preceding claims, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) is epitaxially grown but has a defect or dislocation density higher than  $10^{-10}/\text{cm}^2$ .

14. The substrate (1) of any of the preceding claims, wherein the bulk layer (3) is Si (100).

15. The substrate (1) of any of claims 1-13, wherein the bulk layer (3) is Si(111).

16. The substrate (1) of any of claims 1-15, wherein the buffer layer (4) or the at least the outermost sub-layer (4c) has a different orientation than the bulk layer (3)

17. The substrate (1) of any of claims 1-15, wherein the buffer layer (4) or the sub-layers preserves the orientation of the bulk layer (3).

18. The substrate (1) of any of claims 1-15, wherein the buffer layer (4) or at least one of the sub-layers is polycrystalline.

19. The substrate (1) of any of claims 1-18, wherein the substrate comprises multiple, stacked Bragg reflectors, formed by a plurality of sub-layer, each Bragg reflector reflecting a separate light emitting wavelength.

20. The substrate (1) of any of claims 1-19, which exhibits a wafer curvature less than  $50 \text{ km}^{-1}$ , preferably less than  $40 \text{ km}^{-1}$ .

21. , The substrate (1) of any of claims 1-197, which exhibits a wafer curvature less than  $30 \text{ km}^{-1}$ , preferably less than  $20 \text{ km}^{-1}$ .

22. A structure comprising a substrate in accordance with any of the preceding claims and one or more nanostructures (2) grown on the surface (5) of the buffer layer (4).

23. The structure of claim 22, wherein the nanostructures (2) comprise GaN.

24. The structure of claim 22 or 23, wherein the structure comprises a plurality of nanostructures (1) that are electrically connected by a common lateral contact formed by said buffer layer (4) or at least one of said one or more sub-layers (4a, 4b, 4c).

25. A nanowire LED structure comprising the structure of any of claims 22-24, wherein each nanostructure (2) in use contributes to the formation of an active region for generation of light.

26. The nanowire LED structure of claim 25, wherein each nanostructure comprises a nanowire core and a shell, wherein only the core



constitute a nanostructure, such as a nanowire on which a shell is provided, while the shell has dimensions which are larger than typical nanowire shells.

27. The nanowire LED structure of claim 26, wherein the nanostructures comprise a plurality of facets.

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28. The nanowire LED structure of claim 27, wherein the shells exhibit pyramid facets and/or vertical sidewall facets.

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29. The nanowire LED structure of any of claims 26-28, wherein each individual device has a shape selected from shapes ranging from a pyramid shape, which is narrower at the top or tip and wider at the base, and pillar shaped, which is about the same width at the tip and base.

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30 The nanowire LED structure of any of claims 26-29, wherein each individual device has a circular or hexagonal or other polygonal cross section perpendicular to the long axis of the device.

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31. The nanowire LED structure of any of claims 26-30, wherein the base widths of each individual device range from 100 nm up to 5  $\mu\text{m}$ , preferably 100 nm to below 1 micron, and the heights range from a few 100 nm up to 10  $\mu\text{m}$ .

32. A method (1) for forming a structure comprising a multitude of nanowires oriented in the same direction, wherein the method comprises the steps of:

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- providing a bulk layer (3);
- depositing a buffer layer (4) with a thickness of less than 2 $\mu\text{m}$  on the bulk layer (3); and
- growing one or more nanowire (2) on the buffer layer (4).

33. The method of claim 32, wherein the buffer layer is grown using non-epitaxial materials.

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34. The method of claim 33, wherein the non-epitaxial materials used in the growth of the buffer layer are selected among materials that can withstand the growth temperatures, preferably materials with orientational properties that improve thermal properties of the device.

35. The method of claim 34, wherein the non-epitaxial materials are selected from AlN, TiN, graphene, and other polycrystalline or partly amorphous carbon films.

36. The method of claim 32, wherein the step of depositing a buffer layer (4) comprises depositing one or more sub-layers (4a, 4b, 4c).

37. The method of claim 32 or 33, wherein the deposition of the buffer layer (4) preserves the orientation of the bulk layer (3).

38. The method of claim 32 or 33, wherein the deposition of the buffer layer (4) alters the orientation of the bulk layer (3).

39. The method of any of claims 32-38, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are deposited by LPCVD, APCVD or PECVD.

40. The method of any of claims 32-39, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are deposited by ALD.

41. The method of any of claims 32-40, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are deposited by PVD.

42. The method of any of claims 32-41, wherein the buffer layer (4) or one or more of the sub-layers (4a, 4b, 4c) are grown by MOVPE or HVPE.

43. The method of any of claims 32-42, wherein holes in a mask layer arranged on the buffer layer in accordance with the invention functioning as apertures for nanowire growth is used, and the hole diameter is less than 200nm.

44. The method of any of claims 33-43, wherein the materials deposited for the buffer layer and the sub-layers are selected from the group consisting of a semiconductor material, e.g. a nitride-based III-V semiconductor, a metal or metal alloy, an insulator and graphene.

45. A method of making a nanowire based LED array, comprising providing a substrate as claimed in claim 1,

growing nanowires forming cores for light emitting diodes;

growing shells on said nanowires; wherein

the shapes and sizes of the shells are controlled so as to form shapes ranging

from a pyramid shape, which is narrower at the top or tip and wider at the base, to pillar shaped, which is about the same width at the tip and base.

1/3

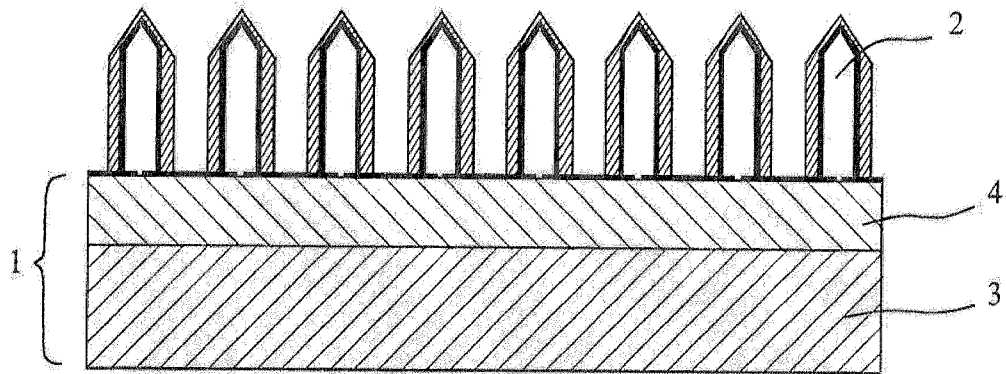


Fig. 1

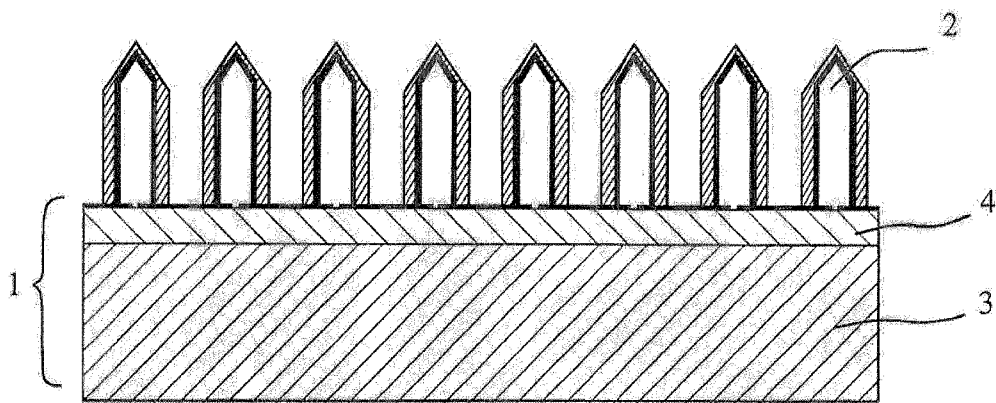


Fig. 2

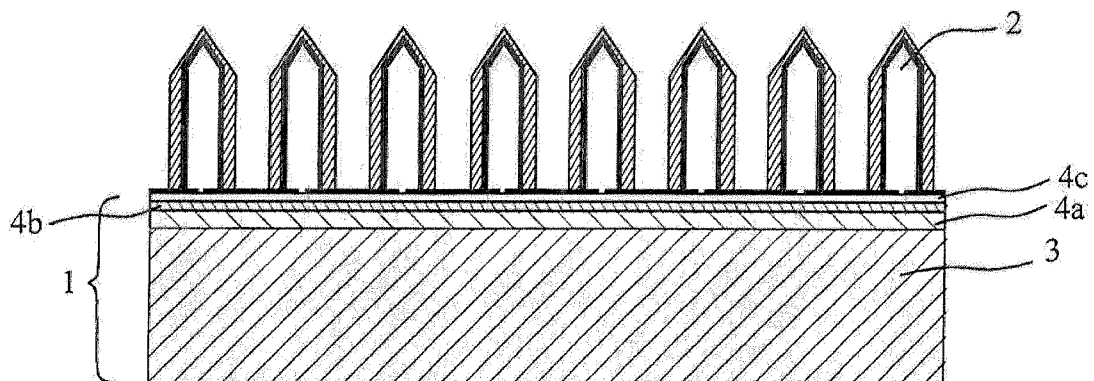


Fig. 3

2/3

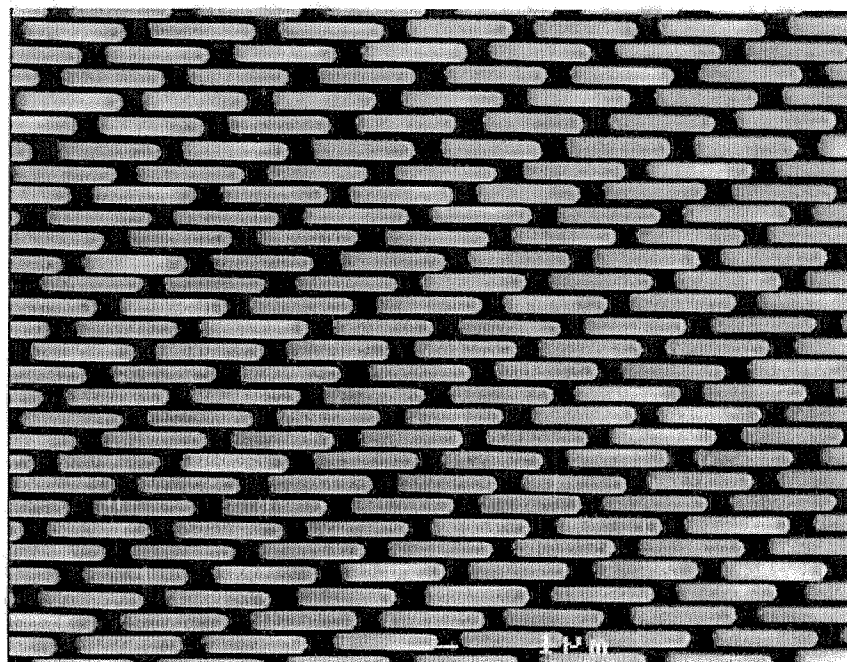


Fig. 4

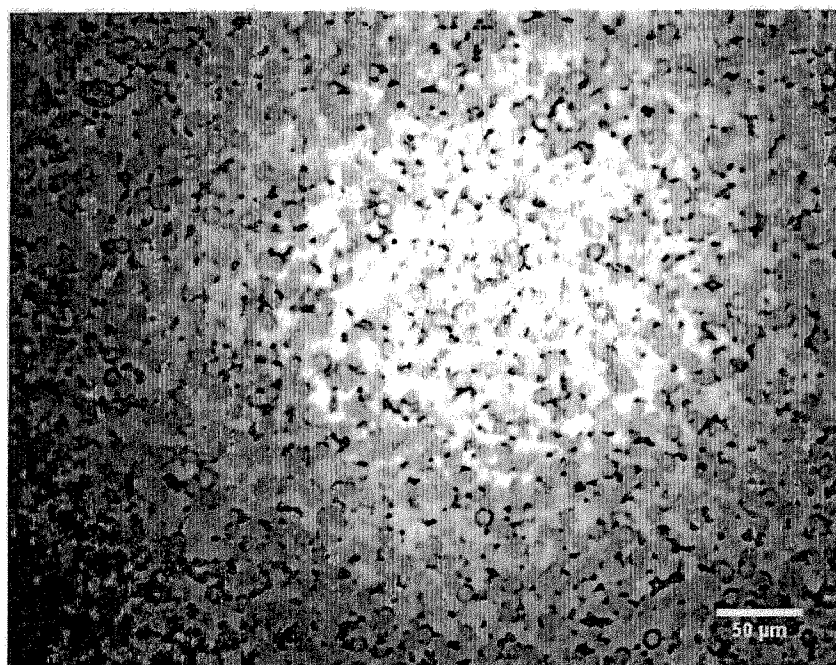


Fig. 5

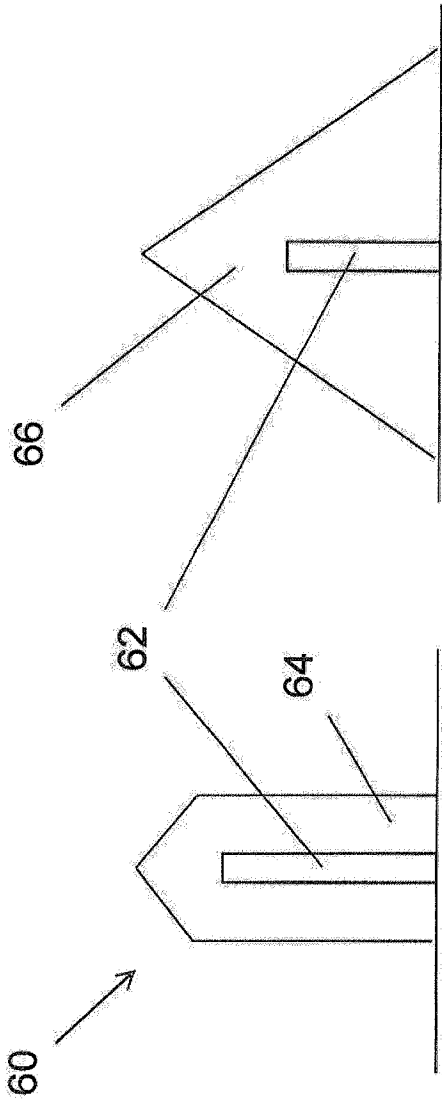


Fig. 6b

Fig. 6a

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SE2011/050845

## A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B82Y, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, COMPENDEX, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20070257264 A1 (HERSEE STEPHEN D ET AL), 8 November 2007 (2007-11-08); abstract; paragraphs [0002]-[0003], [0011], [0025]-[0027], [0029], [0033]-[0034], [0049], [0052]-[0055]; figures 1,4 --	1-2, 4-5, 10, 12-13, 17, 20-25, 37
X	US 20080191191 A1 (KIM HWA MOK), 14 August 2008 (2008-08-14); abstract; paragraphs [0030]-[0032], [0046]-[0055], [0066]; figure 1 --	1-2, 4-5, 10, 12-13, 22-23, 25, 32, 37, 39-43
X	Heon-Jin Choi et al, The role of GaN/AlN double buffer layer in the crystal growth and photoluminescence of GaN nanowires, Chemical Physics Letters 413 (2005) 479-483.; whole document; abstract --	1, 3, 6, 15, 22, 32



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&amp;” document member of the same patent family

Date of the actual completion of the international search

25-11-2011

Date of mailing of the international search report

28-11-2011

Name and mailing address of the ISA/SE

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SE2011/050845

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	O. Landré et al, Growth mechanism of catalyst-free [0001] GaN and AlN nanowires on Si by molecular beam epitaxy, Phys. Status Solidi C 7, No 7-8, sid 2246-2248, 2010-04-30.; whole document; abstract; Chapters 2.1, 3 --	1, 7, 14, 16, 22, 32, 36, 38
X	US 20080036038 A1 (HERSEE STEPHEN D ET AL), 14 February 2008 (2008-02-14); abstract; paragraphs [0054], [0117]-[0118]	1, 11, 22
Y	--	19
Y	W.I.Lee, Wide bandwidth AlAs/AlGaAs tandem Bragg reflectors grown by organometallic vapor phase epitaxy Appl. Phys. Lett. 67, 3753-3755 (1995); whole document; abstract --	19
P, X	Won Mook Choi et al, Selective growth of ZnO nanorods on SiO <sub>2</sub> /Si substrates using a graphene buffer layer, Nano Res, May 2011, 4(5) pages 440-447; whole document; abstract	1, 22
X	--	8
X	Yan-Ru Lin et al, Buffer-Facilitated Epitaxial Growth of ZnO Nanowire, Crystal growth & Design 2005 vol 5, no 2 pages 579-583.; whole document; abstract; Chapters: Introduction, Experimental section --	1, 9
X	WO 2009096932 A1 (GOYAL AMIT), 6 August 2009 (2009-08-06); page 37, paragraph [0007] - paragraph [0013] -- -----	1, 18, 33-35, 44

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SE2011/050845

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional box

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-25, 32-44

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.



**Continuation of:** Box No. III

The following separate inventions were identified:

1: Claims 1-25, 32-44 directed to substrate with buffer layers and a device using the substrate with the buffer layer as starting material to a device comprising nanowires.

2: Claims 26-31, 45 directed to the shape of the nanostructure in a nanowire LED.

A partial search has been carried out, which relates to the invention 1 mentioned above.

The present application has been considered to contain 2 inventions which are not linked such that they form a single general inventive concept, as required by Rule 13 PCT for the following reasons:

The single general concept of the present application is teaching that a substrate with a thin buffer layer (less than 2  $\mu\text{m}$ ) is used for growth of nanowires in order to avoid substrate bowing and hence keeping a uniform thermal profile over the substrate during nanowire growth increasing the manufacturing yield.

The closest prior art has been identified as D1: US 2007257264 A1

Document D1 discloses (abstract, paragraphs [0002]-[0003], [0011], [0025]-[0027], [0029], [0033]-[0034], [0049], [0052]-[0055], figures 1, 4) describes a LED-device comprising nanowires made of GaN, InGaN, AlGaIn or AlInGaIn. The substrate on which the nanowires are deposited is having a buffer layer. The buffer layer has a thickness of 200-600 nm and is made of GaN or AlGaIn

Thus, the single general concept is known and cannot be considered as a single general inventive concept in the sense of Rule 13.1 PCT.

No other features can be distinguished which can be considered as the same or corresponding special technical features in the sense of Rule 13.2 PCT.

**Continuation of:** second sheet

**International Patent Classification (IPC)**

**H01L 29/06** (2006.01)

**B82Y 15/00** (2011.01)

**H01L 21/02** (2006.01)

**H01L 33/12** (2010.01)

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Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SE2011/050845

US	20070257264 A1	08/11/2007	NONE		
US	20080191191 A1	14/08/2008	JP	2008544567 A	04/12/2008
			WO	2007001099 A1	04/01/2007
US	20080036038 A1	14/02/2008	AU	2007313096 A1	24/04/2008
			CA	2643439 A1	24/04/2008
			EP	1994552 A2	26/11/2008
			JP	2009542560 A	03/12/2009
			KR	20090008182 A	21/01/2009
			KR	101019941 B1	09/03/2011
			MX	2008011275 A	25/11/2008
			NZ	570678 A	29/10/2010
			SG	170094 A1	29/04/2011
			US	8039854 B2	18/10/2011
			US	20090169828 A1	02/07/2009
			US	7521274 B2	21/04/2009
			WO	2008048704 A3	03/07/2008
WO	2009096932 A1	06/08/2009	AU	2008349510 A1	06/08/2009
			CA	2745269 A1	06/08/2009
			CN	101981685 A	23/02/2011
			EP	2250664 A1	17/11/2010