

LIGHT EMITTING DIODE AND METHOD FOR MANUFACTURING A LIGHT EMITTING DIODE

Field of the Invention

The present invention relates to light emitting diodes (LEDs) and methods for their manufacture. More particularly, it relates to cubic GaN-based LEDs emitting in the red region of the visible spectrum. LEDs according to the invention are of particular interest for augmented and virtual reality displays (AR/VR), mobile phones, watches, laptops, and televisions.

Background

MicroLED devices are of particular interest for augmented reality (AR) and virtual reality (VR) applications. When reviewed against competing display technologies such as liquid crystal displays (LCD), organic light emitting diodes (OLED) and miniLEDs, microLED offers the greatest potential to balance the need for higher resolution, faster response times, greater contrast ratios and lower energy consumption.

The small size of microLEDs means that many more can be produced on a single wafer than larger, conventional LEDs. This results in a higher device yield per wafer, and consequently can drive down unit costs. Additionally, the ability to drive microLED devices locally enables the production of 'bezel-free' displays, offering consumers a more immersive viewing experience with an edge-to-edge screen. High yields and bezel-free designs are also highly desirable as they allow displays to be "tiled" together to give very large displays.

Despite their prospective benefits, there are still outstanding issues with microLED display technologies that require resolving. There are signs that the improvements in performance available from squeezing conventional devices are dwindling. It is of particular interest to take an approach which provides advantages over existing technology but which can be used in existing manufacturing lines without radical redesign of those manufacturing lines.

A significant amount of LED research has focussed on the h-InGaN (hexagonal indium gallium nitride) system which has delivered rapid improvements in LED performance over its relatively short 30-year lifetime to date. However, there are signs that the rate of progress is slowing. The technical reasons behind the deterioration in h-InGaN LED efficiency at longer wavelengths are well-documented and understood. They relate primarily to the existence of a large, internal electric field that arises from the asymmetry of the hexagonal crystal structure in certain directions. The electric field extends across the quantum wells (QWs) that form the active region of the LED, irrespective of the size of the device. The electric field tends to separate the electrons and holes in the QWs and reduce the rate of radiative

recombination, the process which is fundamental to the emission of light from the device. This situation is exacerbated by increasing the indium content of the QWs, a necessity if longer wavelength emissions such as green, amber and red are desired. Also, increased indium increases strain in the crystal structure, resulting in even stronger electric fields due to the piezoelectric effect, impacting further on efficiency. As a result of these internal electric fields the width of the QWs that can be employed in h-InGaN based devices is limited to 2 to 3nm, placing a further constraint on the tools that device designers could use to access longer wavelengths.

The present invention has been devised in light of the above considerations.

Summary of the Invention

Approaches trying to address the issues with producing long-wavelength microLEDs with the h-InGaN system have focussed on trying to move the electric field into a direction that does not interfere with the radiative recombination process in the QWs. This can be achieved by rotating the crystal structure with respect to the device. This can be done by growing the structure on a substrate with its surface cut parallel to a crystal plane at a significant angle to the c-plane usually employed for h-InGaN LEDs. These are known as semi-polar and non-polar h-GaN according to whether the crystal orientation chosen merely reduces or completely removes the electric fields.

Unfortunately, while this helps with the problems caused by the internal electric fields, it does not address all the challenges of producing long wavelength LEDs. For example, it has been found that growing high-quality InGaN Q-wells with high indium content is extremely challenging due to the GaN/InN immiscibility gap and for some orientations, particularly non-polar GaN this is exacerbated. Also, the availability of large-area, low-cost substrates for high-volume manufacture is restricted for some desirable semi-polar crystal orientations. In addition, moving to non-c-plane h-GaN orientations results in a requirement to manage additional defects that appear in the grown layers. Managing these trade-offs between these conflicting factors is difficult and despite significant investment and considerable effort, these approaches have yielded limited progress towards a viable production technology for efficient h-InGaN LEDs in the green, amber and red regions of the spectrum.

Additionally, there is a large efficiency drop when devices are miniaturised to the scale required for microLED applications. Currently, small-form red LEDs are made in the aluminium-indium-gallium phosphide (AlInGaP) system. At a large enough scale these can exhibit an efficiency of around 60%. Unfortunately, this efficiency drops sharply when the device area is shrunk; at a diameter of 5µm the efficiency sinks to a few percent – whereas for blue LEDs in the GaN-based system can maintain efficiencies of around 40%.

In the light of these limitations to the performance of long wavelength hex-GaN and AlInGaP microLEDs, the present inventors have considered a different approach.

The present disclosure is based on the inventors' insights into cubic GaN-based material, in contrast to
5 the large amount of research effort carried out on hexagonal GaN-based material. The use of cubic GaN-based material is known to have several basic advantages, including avoiding the internal electric fields associated with h-GaN, reducing the band gap by about 200meV and providing a route to increase the hole mobility and the maximum achievable hole concentration. If these advantages could be brought together, this would allow longer wavelength LEDs that maintain higher efficiency even at small device
10 areas. However, even with the benefit of prior work on cubic GaN, it has remained difficult to achieve satisfactory red wavelength emission in a microLED in the cubic GaN system.

Accordingly, in a first aspect, the present invention provides a light emitting diode comprising:

- an n-type cubic GaN-based layer;
 - 15 a p-type cubic GaN-based layer;
 - an active region formed between the n-type and p-type cubic GaN-based layers;
- wherein:
- the active region comprises at least one quantum well formed of cubic $\text{In}_x\text{Ga}_{1-x}\text{N}$ -based material with thickness t_{QW} ;
 - 20 the in-plane area of the active region is not more than $10,000 \mu\text{m}^2$;
 - the light emitting diode has an electroluminescence peak wavelength in the range 600-750 nm;
- and
- the thickness t_{QW} and indium content x satisfy the following relationships:
- 25 $t_{\text{QW}} \geq 2.5 \text{ nm}$
 - $t_{\text{QW}} \leq 10 \text{ nm}$
 - $x \geq 0.1$
 - $x \leq 0.5$

The present inventors have found that with this approach it is possible to manufacture a cubic GaN-based
30 microLED that emits red visible light.

In a second aspect, the present invention provides a light emitting device array comprising at least one pixel itself comprising at least three sub-pixels, being a red sub pixel formed of a cubic GaN-based LED and being according to the first aspect, a green sub-pixel formed of a GaN-based LED, and a blue sub-
35 pixel formed of a GaN-based LED.

In a third aspect, the present invention provides a method for manufacturing a light emitting diode according to any of the previous aspects, comprising the steps:

- providing a (001) silicon wafer substrate with a (001) 3C-SiC epitaxial layer;
- growing a cubic GaN-based epitaxial buffer layer on the (001) 3C-SiC epitaxial layer;
- epitaxially growing the n-type cubic GaN-based layer;
- epitaxially growing the active region on the n-type cubic GaN-based layer;
- 5 epitaxially growing the p-type cubic GaN-based layer on the active region.

Optional features of the invention are now set out, these being applicable singly or in any combination with any aspect of the invention, unless the context demands otherwise.

- 10 The LED may have a peak electroluminescence wavelength that varies according to the following equation:

$$\text{electroluminescence peak wavelength} = xt_{\text{QW}}(Ax + B) + C$$

where:

A is a dimensionless number in the range 90-125

- 15 B is a dimensionless number in the range 50-95

C is the near band edge (NBE) wavelength of cubic gallium nitride, expressed in nm.

- This empirical equation is based on modelling indicating the expected change in peak electroluminescence wavelength with indium content (x) and thickness of the quantum wells (t_{QW}). These parameters and the additional parameters set out in the equation will now be discussed in more detail.
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- It is considered that increasing the thickness t_{QW} of the quantum well(s) may permit increasing peak electroluminescence wavelength for the same indium content. Accordingly, to achieve the desired emission wavelength, t_{QW} may be ≥ 3.0 nm, ≥ 3.5 nm, ≥ 4.0 nm, ≥ 4.5 nm, ≥ 5.0 nm, ≥ 5.5 nm, ≥ 6.0 nm, ≥ 6.5 nm, ≥ 7.0 nm. However, with increasing thickness of the quantum wells, increasing stress is introduced into the device. If this stress exceeds the critical stress for the introduction of defects this will reduced device efficiency. Accordingly, t_{QW} may be, ≤ 9.5 nm, ≤ 9.0 nm, ≤ 8.5 nm, ≤ 8.0 nm, ≤ 7.5 nm, ≤ 7.0 nm, ≤ 6.5 nm, ≤ 6.0 nm. Any recited lower end point may be combined with any recited upper end point to provide a practical range.
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C, the near band edge (NBE) wavelength of cubic gallium nitride, depends to an extent on the strain state and temperature of the cubic gallium nitride and may typically lie in the range 375-395 nm. For the purposes of exemplary application of the empirical equation, a value of C of 385 nm may be selected.

A and B arise as numerical factors in an analysis of lines of best fit for the modelling data described later. A is at least 90 and may be at least 92, at least 94, at least 96, at least 98, at least 100, at least 102, at least 104, or at least 106. A is at most 125 and may be at most 124, at most 122, at most 120, at most 118, at most 116, at most 114, at most 112, or at most 110. Any recited lower end point may be combined with any recited upper end point to provide a practical range.

B is at least 50 and may be at least 52, at least 54, at least 56, at least 58, at least 60, at least 62, at least 66, at least 68, or at least 70. B is at most 95 and may be at most 94, at most 92, at most 90, at most 88, at most 86, at most 84, at most 82, or at most 80. Any recited lower end point may be combined with any recited upper end point to provide a practical range.

Any available range for A may be used in combination with any available range for B. For example, A may be in the range $A = 100\text{--}115$ and B may be in the range $B = 60\text{--}85$. As another example, A may be in the range $A = 105\text{--}110$ and B may be in the range $B = 70\text{--}75$.

The indium fraction x in the quantum wells has an effect on peak electroluminescence wavelength. Increasing x tends to provide an increase in wavelength. However, with increasing x there is also increasing strain in the quantum wells, and therefore increasing strain is introduced into the device, leading to the potential for a greater concentration of defects which can result in reduced device efficiency. Indium content x to achieve the desired emission wavelength is at least 0.1. In some embodiments, x is at least 0.12, at least 0.14, at least 0.16, at least 0.18, at least 0.2, at least 0.22, at least 0.24, at least 0.26, at least 0.28, at least 0.3, at least 0.32, at least 0.34, at least 0.36, at least 0.38, or at least 0.4. Indium content x is at most 0.5. In some embodiments, x is at most 0.48, at most 0.46, at most 0.44, at most 0.42, at most 0.40, at most 0.38, at most 0.36, at most 0.34, at most 0.32, at most 0.3, at most 0.28, at most 0.26, at most 0.24, at most 0.22, or at most 0.2. Any recited lower end point may be combined with any recited upper end point to provide a practical range. In some embodiments, x is in the range 0.15–0.45. In some embodiments, x is in the range 0.2–0.45. In some embodiments, x is in the range 0.25–0.45. In some embodiments, x is in the range 0.3–0.45.

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At an early stage in device research, the external quantum efficiency of new class LEDs may be relatively low. For example, the external quantum efficiency may be at least 0.1%. It is recognised that this is typically not acceptable for commercial devices but can be subject to further device improvement. For example the external quantum efficiency of the LED may be at least 0.5%, at least 1%, at least 2%, at least 5%, at least 10%, at least 15%, at least 20% at least 25%, at least 30%, at least 35%, or at least 40%.

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The active region has an in-plane area of not more than $10,000 \mu\text{m}^2$. By "in-plane", it is intended to refer to the area of a plane that is parallel to and coincident with the quantum well (or one of the quantum wells) of the active region, on the assumption that the quantum well is itself satisfactorily planar. For example, the active region may be in the form of a circle, square, rectangle or other suitable shape. As will be understood, the active region may have a square shape of sides up to $100 \mu\text{m}$. The active region may have an in-plane area of not more than $8,000 \mu\text{m}^2$, not more than $6,000 \mu\text{m}^2$, not more than $4,000 \mu\text{m}^2$, not more than $3,000 \mu\text{m}^2$, not more than $2500 \mu\text{m}^2$, not more than $2000 \mu\text{m}^2$, not more than $1500 \mu\text{m}^2$, or not more than $1000 \mu\text{m}^2$,. As will be appreciated in the light of this disclosure, as the in-plane area of the active region decreases, the challenges explained above in relation to device efficiency become more challenging and therefore the benefits of the present invention become more apparent.

The active region may have a smallest in-plane dimension of at least $0.1 \mu\text{m}$. The active region may have a smallest in-plane dimension of at least $0.5 \mu\text{m}$, at least $1 \mu\text{m}$, at least $2 \mu\text{m}$, at least $3 \mu\text{m}$, at least $4 \mu\text{m}$, or at least $5 \mu\text{m}$. The active region may have a largest in-plane dimension of at most $100 \mu\text{m}$, at most $50 \mu\text{m}$, at most $40 \mu\text{m}$, at most $30 \mu\text{m}$, at most $20 \mu\text{m}$, at most $15 \mu\text{m}$, or at most $10 \mu\text{m}$. For the active region, the ratio between the largest in-plane dimension and the smallest in-plane dimension may be at most 20, at most 15, at most 10, at most 9, at most 8, at most 7, at most 6, at most 5, at most 4, at most 3, at most 2, or at most 1.5.

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At least one of the n-type cubic GaN-based layer, the active region and the p-type cubic GaN-based layer may be at least 90% cubic. This may be measured using X-ray diffraction techniques discussed below. At least one of the n-type cubic GaN-based layer, the active region and the p-type cubic GaN-based layer may be at least 92% cubic, at least 94% cubic, at least 95% cubic, at least 96% cubic, at least 97% cubic, at least 98% cubic, at least 99% cubic, at least 99.5% cubic, or at least 99.9% cubic. These ranges may apply to two or all of the n-type cubic GaN-based layer, the active region and the p-type cubic GaN-based layer.

The LED may be configured such that the electroluminescence peak lies in the range of 600 to 700 nm. In some embodiments, the electroluminescence peak lies in the range of 610 to 675 nm. In some embodiments, the electroluminescence peak lies in the range of 620 to 650 nm.

The LED is configured such that it contains at least one quantum well. The LED may contain at least two, at least three, at least four, at least five, at least six, at least seven, at least eight, or at least nine quantum wells. In some embodiments, there may for example be from two to five quantum wells. For such multiple quantum well structures, there may be cubic GaN-based quantum barriers between adjacent quantum wells.

The LED may be configured such that the thickness of the cubic GaN-based buffer layer is at least 1 μm . This thickness may be at least 1.5 μm , at least 2 μm , or at least 2.5 μm .

- 5 The LED may be configured such that the electroluminescence peak wavelength in the range of 600-750nm has a FWHM of not more than 90nm. This FWHM may be not more than 80nm, not more than 70nm, not more than 60nm, or not more than 50nm.

- 10 In the context of the second aspect, the height of each sub-pixel may be substantially the same. For example, the respective heights of the sub-pixels may be within 30% of each other, or within 20% of each other, or within 10% of each other.

- 15 In the context of the third aspect, the (001) silicon wafer substrate may have a diameter of 100mm or larger, or 150mm or larger, for example about 300mm is particularly suitable for industrial scale manufacture.

- In the embodiments of the invention, a substantially (001) oriented zincblende structure (i.e. cubic) group III-nitride layer in manufactured by a method including the steps:
- providing a silicon substrate;
- 20 providing a 3C-SiC layer on the silicon substrate;
- growing a group III-nitride nucleation layer;
- carrying out a nucleation layer recrystallization step; and
- depositing and growing the zincblende structure group III-nitride layer by MOVPE at temperature T3 in the range 750-1000 °C, to a thickness of at least 0.3 μm .

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- These steps have been found to provide a zincblende structure group III-nitride layer of improved crystalline quality, in particular with respect to the reduction of the formation of wurtzite structure (i.e. hexagonal) group III-nitride inclusions.
- 30 In this disclosure, some numerical ranges are expressed in terms of open ended ranges with upper or lower limits, or in terms of closed ended ranges with upper and lower limits. It is expressly stated here that preferred ranges are disclosed herein that are combinations of upper and/or lower limits from different ranges for the same parameter.

- Preferably, before growing the group III-nitride nucleation layer, the 3C-SiC layer is subjected to a nitridation step at a temperature T1 in the range 800-1100 °C. This step is considered to be advantageous in terms of ensuring the plentiful availability of N for subsequent group III-nitride formation.
- 5 The use of temperature T1 outside this range is considered to reduce the PL NBE peak intensity and broadens the emission FWHM.

- We now consider the conditions for deposition and growth of the group III-nitride nucleation layer. Preferably, the group III-nitride nucleation layer is grown at temperature T2 in the range 500-700 °C.
- 10 More preferably, the temperature T2 is in the range 550-650 °C. The growth rate may be at least 0.1 nm/s. The growth rate may be up to 1 nm/s. The thickness of the nucleation layer may be at least 3 nm, but is more preferably greater than 3 nm. More preferably, the thickness of the NL may be at least 10nm. The thickness of the nucleation layer (NL) may be up to 100nm. Preferably, the thickness of the NL may be up to 50nm. More preferably, the thickness of the NL may be up to 40nm. Preferably, the chosen
- 15 temperature for T2 lies about 40-60 °C above the temperature where the growth rate deviates from a constant value to a lower value, entering a regime in which the ammonia flow determines the growth rate.

- Following the growth of the nucleation layer, there is the nucleation layer recrystallization step. In this step, preferably the temperature is ramped up at a rate of between 0.1-10 °C/second. More preferably
- 20 the temperature is ramped up at a rate of between 0.5-5 °C/second. This is found to be a suitable approach for satisfactory nucleation layer recrystallization, permitting subsequent high quality epilayer deposition.

- The group III-nitride nucleation layer is preferably a zincblende structure group III-nitride nucleation layer.
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- In the step of depositing and growing the zincblende structure group III-nitride layer on the recrystallized nucleation layer, the reactor pressure is preferably not more than 500 Torr. More preferably, the reactor pressure is not more than 300 Torr. More preferably, the reactor pressure is not more than 100 Torr.
- 30 In the step of depositing and growing the zincblende structure group III-nitride layer on the recrystallized nucleation layer, the V-to-III ratio is preferably in the range 10-300. More preferably, the V-to-III ratio is in the range 20-150. More preferably the V-to-III ratio is in the range 50-100. During this step, the growth rate is preferably in the range 0.1-1 nm/second. A growth rate of about 0.5 nm/second has been found to be suitable, for example. Careful selection of the V-to-III ratio within the preferred ranges shows
- 35 improvements in the surface morphology, the zincblende phase purity and XRD rocking curve peak widths.

In the step of depositing and growing the zincblende structure group III-nitride layer on the recrystallized nucleation layer temperature T3 is preferably in the range 800-920 °C. More preferably, temperature T3 is at least 810 °C, more preferably at least 820 °C, more preferably at least 830 °C. Temperature T3 is preferably at most 910 °C, at most 900 °C, or at most 890 °C. A particularly suitable range for T3 is found to be 845-880 °C. Careful selection of temperature T3 within the preferred ranges shows improvements in the surface morphology from Nomarski images, XRD rocking curve peak width and PL. For example, samples grown in the range 860 -880 °C shows a relatively smooth surface and corresponding NBE PL peak is the strongest, although also the broadest in the data presented here. At higher growth temperature, it is found that the surface roughens, the PL NBE peak narrows significantly but also the yellow band increases in intensity.

Changes in surface roughness with growth temperature were confirmed from AFM. The phase purity, as determined by XRD shows that it is possible to very substantially reduce the amount of wurtzite inclusions when T3 is 900 °C or lower. When T3 is higher than 900 °C the XRD analysis shows an increasing contribution of reflections due to the wurtzite lattice, indicating incorporation of hexagonal inclusions in the cubic zincblende matrix.

It has been found that it is possible to widen the preferred conditions of temperature T3 and III-V ratio by carrying out epilayer growth at relatively low pressure. In one exemplary set of conditions for growing zincblende GaN epilayers by MOVPE at a constant pressure of 100 Torr, T3 can be in the range 850 and 890 °C, with a V/III ratio of 38 to 150. This results in a relatively smooth film with a wurtzite contamination of less than 1%. The preferred thickness of the NL is in the range 10-50 nm, for example about 22nm.

Preferably, the group III-nitride layer is an $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ based layer, where $0 \leq x \leq 1$, $0 \leq y \leq 1$.

The silicon substrate has a diameter of at least 100mm. Different substrate diameters are possible. It is notable that the growth processes described here are easily scalable to substrates of any suitable size, such as at least 150mm, at least 200mm or at least 300mm.

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In the present disclosure, the semiconductor structure may comprise a zincblende structure group III-nitride layer, wherein:

the group III-nitride layer has a thickness of at least 0.5 μm ; and

the group III-nitride layer is monocrystalline zincblende structure group III-nitride to the extent that when the group III-nitride layer is subjected to XRD characterization, the intensity I_{10-11} attributable to wurtzite

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structure group III-nitride 10-11 reflections and the intensity I_{002} attributable to zincblende structure group III-nitride 002 reflections satisfy the relation:

$$\frac{I_{10-11}}{I_{002}} \leq 0.10$$

5 Preferably, at least one of the following relationships applies:

$$\frac{I_{10-11}}{I_{002}} \leq 0.08$$

$$\frac{I_{10-11}}{I_{002}} \leq 0.06$$

$$\frac{I_{10-11}}{I_{002}} \leq 0.05$$

$$\frac{I_{10-11}}{I_{002}} \leq 0.04$$

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$$\frac{I_{10-11}}{I_{002}} \leq 0.03$$

$$\frac{I_{10-11}}{I_{002}} \leq 0.02$$

$$\frac{I_{10-11}}{I_{002}} \leq 0.01$$

15 More preferably, the intensity I_{10-11} attributable to wurtzite structure group III-nitride 10-11 reflections and the intensity I_{002} attributable to zincblende structure group III-nitride 002 reflections satisfy the relation:

$$\frac{I_{10-11}}{I_{002}} \leq 0.005$$

20 It is possible for the intensity I_{10-11} attributable to wurtzite structure group III-nitride 10-11 reflections and the intensity I_{002} attributable to zincblende structure group III-nitride 002 reflections to be determined by two dimensional reciprocal space mapping, to form a measured reciprocal space map, encompassing the expected reflections of zincblende structure group III-nitride 002 and wurtzite structure group III-nitride 10-11. Reciprocal space mapping is a technique that is well known to the skilled person and allows an efficient capture of a large amount of data to indicate the crystal phases present in the film.

25 The intensity I_{10-11} located at a position in reciprocal space attributable to wurtzite structure group III-nitride 10-11 reflections may be caused by stacking faults formed on {111} facets of zincblende structure group III-nitride, evidenced by elongate streaks in the measured reciprocal space map between the reflections of zincblende structure group III-nitride 002 and the expected wurtzite structure group III-nitride 10-11 reflections. In this way, it is possible for there to be measurable reflected x-ray intensity at the
30 defined location in reciprocal space, but this does not necessarily mean that wurtzite structure group III-

nitride inclusions are present. Rather, the x-ray intensity may be provided by reflections from stacking faults. The presence of hexagonal stacking faults is considered to be less problematic to the performance of the group III nitride layer than the presence of wurtzite structure inclusions.

- 5 Also discloses herein is a zincblende structure group III-nitride layer, such as part of a semiconductor device, wherein:

the group III-nitride layer has a thickness of at least 0.5 μm ; and

the group III-nitride layer is monocrystalline zincblende structure group III-nitride to the extent that when the group III-nitride layer is subjected to XRD characterization, the relative volume proportions of

- 10 zincblende structure group III-nitride V_{zb} and wurtzite structure group III-nitride V_{wz} satisfy the relation:

$$\frac{V_{wz}}{V_{zb}} \leq 0.10$$

where V_{wz} is assessed on the basis of wurtzite structure group III-nitride 1-103 reflections and V_{zb} is assessed on the basis of zincblende structure group III-nitride 113 reflections according to:

$$\frac{V_{wz}}{V_{zb}} = \frac{I_{1-13}}{I_{113}} \cdot \frac{1 + \cos^2(2\theta_{113})}{1 + \cos^2(2\theta_{1-13})} \cdot \frac{2 \cdot \sin(\theta_{1-13}) \cdot \cos(\theta_{1-13})}{2 \cdot \sin(\theta_{113}) \cdot \cos(\theta_{113})} \cdot \frac{\left(\frac{|F_{113}|}{V_{uczb}}\right)^2}{\left(\frac{|F_{1-13}|}{V_{ucwz}}\right)^2}$$

- 15 where:

V_{uczb} is the volume of the zincblende structure group III-nitride unit cell

V_{ucwz} is the volume of the wurtzite structure group III-nitride unit cell

F_{113} is the structure amplitude of the zincblende structure group III-nitride 113 reflections

F_{1-13} is the structure amplitude of the wurtzite structure group III-nitride 1-103 reflections

- 20 $2\theta_{113}$ is the 2θ angle for the zincblende structure group III-nitride 113 reflections

$2\theta_{1-13}$ is the 2θ angle for the wurtzite structure group III-nitride 1-103 reflections

I_{113} is the integrated intensity of the zincblende structure group III-nitride 113 reflections

I_{1-13} is the integrated intensity of the wurtzite structure group III-nitride 1-103 reflections.

- 25 Preferably, at least one of the following relationships applies:

$$\frac{V_{wz}}{V_{zb}} \leq 0.08$$

$$\frac{V_{wz}}{V_{zb}} \leq 0.06$$

$$\frac{V_{wz}}{V_{zb}} \leq 0.05$$

$$\frac{V_{wz}}{V_{zb}} \leq 0.04$$

$$\frac{V_{wz}}{V_{zb}} \leq 0.03$$

$$\frac{V_{wz}}{V_{zb}} \leq 0.02$$

$$\frac{V_{wz}}{V_{zb}} \leq 0.01$$

$$5 \quad \frac{V_{wz}}{V_{zb}} \leq 0.005$$

The zincblende structure group III-nitride layer may be substantially (001) oriented.

10 The zincblende structure group III-nitride layer may have a thickness of at least 0.3 μm . The zincblende structure group III-nitride layer may have a thickness of at least 0.4 μm , at least 0.6 μm , at least 0.8 μm , at least 1 μm , at least 1.5 μm , or at least 2 μm .

15 There may be a reflective layer, such as a distributed Bragg reflector (DBR) or single layer with different refractive index, interposed between the zincblende structure group III-nitride layer and a substrate. This is useful for the structure in use as a device, particular in a light emitting device.

The invention includes the combination of the aspects and optional features described except where such a combination is clearly impermissible or expressly avoided.

20 Summary of the Figures

Embodiments and experiments illustrating the principles of the invention will now be discussed with reference to the accompanying figures in which:

25 Figure 1 shows a top-down view of cubic-InGaN LEDs produced using MOCVD and demonstrates emission in green (bottom), amber (middle) and red (top).

Figure 2 shows a false colour (in the original) nanodiffraction mapping image of a portion of a gallium nitride thin film, indicating a mixture of hexagonal (green) and cubic (red) phases.

30 Figure 3 shows a corresponding X-ray diffraction analysis for the sample of Figure 2, indicating a mixture of hexagonal and cubic phases.

Figure 4 shows a false colour (in the original) nanodiffraction mapping image of a portion of another gallium nitride thin film, indicating high cubic (red) phase purity.

- 5 Figure 5 shows a corresponding X-ray diffraction analysis for the sample of Figure 4, confirming high cubic phase purity.

- 10 Figure 6 shows a peak photoluminescence wavelength map across a 150mm n-type c-GaN wafer. In the original, false colour is used to indicate the peak photoluminescence wavelength according to the vertical scale, but note that the colours used do not correspond to the colour of the peak photoluminescence wavelength.

Figure 7 shows the near-band edge photoluminescence spectrum from a point at approximately half radius on the 150mm n-type c-GaN wafer in Figure 6.

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Figure 8 shows I/V curves for different C-TLM Gaps processed on the 150mm n-type c-GaN wafer in Figure 6.

- 20 Figure 9 shows a cross sectional TEM image of a multiple quantum-well (MQW) active region formed on a buffer layer.

Figure 10 shows the photoluminescence peak of a 10nm wide cubic InGaN quantum well with approximately 10% indium (x approximately 0.1).

- 25 Figure 11 shows how the emission wavelength and the integrated photoluminescence intensity vary with quantum well thickness for cubic GaN / InGaN quantum well with approximately 10% indium.

Figure 12 schematically depicts an embodiment of the invention showing the ordering of the layers. [Not to scale.]

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Figure 13 shows an image of a cubic GaN-based LED emitting light with an emission peak at 530 nm.

Figure 14 shows the electroluminescence emission plot corresponding to the LED shown in Figure 13.

Figure 15 shows an image of a cubic GaN-based LED emitting light with an emission peak at 600 nm.

5 Figure 16 shows the electroluminescence emission plot corresponding to the LED shown in Figure 15.

Figure 17 shows how the full-width half maximum (FWHM) varies with the integrated power of a cubic GaN-based LED with an emission peak of 560nm.

10 Figure 18 shows a photomicrograph of a biased cubic GaN-based LED with an emission peak of 560nm.

Figure 19 shows the electroluminescence emission plot corresponding to the LED shown in Figure 18.

15 Figure 20 shows a near-band edge photoluminescence spectrum from a 500nm cubic GaN-based layer on a 1 μ m AlGaIn buffer layer.

Figure 21 shows a graph of the variation in internal quantum efficiency (IQE) across a single c-GaN device, where the vertical axis shows the number of data points with a specific value of IQE.

20 Figure 22 shows the photoluminescence response (note the log scale) from a single point on a 150mm c-GaN LED wafer. The sharp peaks at approximately 530nm and 810nm are measurement artefacts.

25 Figure 23 shows a photoluminescence map of the peak emission wavelength across the 150mm wafer of Figure 22, indicating the variability in peak emission wavelength in early experimental results leading to the present disclosure.

Figure 24 shows an intensity map of the peak emission wavelength across the 150mm wafer of Figure 22.

30 Figure 25 shows a photoluminescence map of the peak emission wavelength across a 150mm wafer., indicating the variability in peak emission wavelength in early experimental results leading to the present disclosure.

Figure 26 shows the photoluminescence response from a single point on the 150mm wafer of Figure 25.

Figure 27 shows surface morphology from a Nomarski differential interference-contrast image of a
5 sample with a single quantum well grown on a cubic GaN buffer layer.

Figure 28 shows a corresponding photoluminescence emission plot for the single quantum well structure in Figure 27 – exhibiting a peak emission wavelength of 580nm.

10 Figure 29 shows surface morphology from a Nomarski differential interference-contrast image of sample with a single quantum well grown on a cubic GaN buffer layer.

Figure 30 shows a corresponding photoluminescence emission plot of the single quantum well structure in Figure 29 – exhibiting a peak emission wavelength of 605nm.

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Figure 31 shows an image of a biased red microLED (with a radius of 25µm).

Figure 32 shows the corresponding electroluminescence emission plot for the microLED in Figure 31 – exhibiting a peak emission wavelength of 612nm.

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Figure 33 shows an image of a biased red microLED (with a radius of 25µm).

Figure 34 shows the corresponding electroluminescence emission plot for the microLED in Figure 33 – exhibiting a peak emission wavelength of 610nm.

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Figure 35 shows an image of a biased red microLED (with a radius of 25µm).

Figure 36 shows the corresponding electroluminescence emission plot for the microLED in Figure 35 – exhibiting a peak emission wavelength of 648nm.

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Figure 37 shows an image of a biased red microLED (with a radius of 50µm).

Figure 38 shows the corresponding electroluminescence emission plot for the microLED in Figure 37 – exhibiting a peak emission wavelength of 624nm.

- 5 Figure 39 shows an image of a biased red microLED (with a radius of 50µm).

Figure 40 shows the corresponding electroluminescence emission plot for the microLED in Figure 39 – exhibiting a peak emission wavelength of 631nm.

- 10 Figure 41 shows an image of a biased yellow microLED (with a radius of 25µm).

Figure 42 shows the corresponding electroluminescence emission plot for the microLED in Figure 41 – exhibiting a peak emission wavelength of 562nm.

- 15 Figure 43 shows an image of a biased red microLED (with a radius of 25µm).

Figure 44 shows the corresponding electroluminescence emission plot for the microLED in Figure 43 plot – exhibiting a peak emission wavelength of 609nm.

- 20 Figure 45 shows an image of a biased red microLED (with a radius of 25µm).

Figure 46 shows the corresponding electroluminescence emission plot for the microLED in Figure 45 – exhibiting a peak emission wavelength of 616nm.

- 25 Figure 47 shows an image of a biased red microLED (with a radius of 25µm).

Figure 48 shows the corresponding electroluminescence emission plot for the microLED in Figure 47 – exhibiting a red peak emission wavelength of 600nm.

- 30 Figure 49 shows how the raw peak efficiencies vary with wavelength for a batch of samples.

Figure 50 shows the predicted variation of wavelength with indium fraction and quantum well thickness in cubic GaN-based LEDs.

Figure 51 shows a modified version of Fig. 50. The shaded region defines the parameter space set in the empirical equation for a quantum well thickness of 8nm and when A and B are at the maximum and minimum values in the following ranges: A = 90-125 and B = 50-95.

Figure 52 shows another modified version of Fig. 50. The shaded region defines the parameter space set in the empirical equation for a quantum well thickness of 8nm and when A and B are at the maximum and minimum values in the following ranges: A = 100-115 and B = 60-85.

Figure 53 shows another modified version of Fig. 50. The shaded region defines the parameter space set in the empirical equation for a quantum well thickness of 8nm and when A and B are at the maximum and minimum values in the following ranges: A = 105-110 and B = 70-75.

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Figure 54 shows another modified version of Fig. 50. The shaded region defines the parameter space set in the empirical equation for a quantum well thickness of 10nm and when A and B are at the maximum and minimum values in the following ranges: A = 90-125 and B = 50-95.

20 Detailed Description of the Invention

Aspects and embodiments of the present invention will now be discussed with reference to the accompanying figures. Further aspects and embodiments will be apparent to those skilled in the art. All documents mentioned in this text are incorporated herein by reference.

25 The present invention draws on developments made by the inventors' research group and disclosed in WO 2018/178315 A1 and in Binks et al (2022) [see full citation below]. WO 2018/178315 A1 provides detailed disclosure on suitable processing conditions for growing epitaxial cubic GaN-based materials on Si-SiC substrates and on characterization techniques for assessing the phase purity of the epitaxial cubic GaN-based materials. Binks et al (2022) presents a review of previous work and also presents additional results on the developments in cubic GaN and InGaN/GaN quantum wells. The entire contents of each of these documents is incorporated by reference in its entirety.

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The disclosure set out here aims to build on the previous work to develop cubic GaN-based LEDs that emit preferentially in the red region of the visible spectrum and which have a small size, in order to take advantage of the device benefits set out above.

- 5 With respect to details of the processing methods used to grow cubic GaN-based epitaxial layers on suitable substrates, we refer to the disclosure of WO 2018/178315 A1 and also to the same document for suitable examples that are characterized to demonstrate suitable cubic phase purity for the GaN-based epitaxial layers.
- 10 Additional experimental details in relation to the present disclosure, such as the formation of suitable quantum wells and the measurement of electroluminescent and photoluminescent response are set out further below.

Efficiency of various GaN LEDs

- 15 **Figure 1** shows light emission from biased cubic-InGaN LEDs produced using metal-organic chemical vapour deposition (MOCVD). The top picture is that of a red cubic GaN LED, the middle is that of a yellow cubic GaN LED and the bottom is that of a green cubic GaN LED. The images show red being the dimmest LED and green being the brightest. This illustrates the difficulties involved when producing longer wavelength GaN LEDs. It is understood that in the context of both macro-sized LEDs and
- 20 microLEDs longer wavelength emission can be achieved in two ways:
1. Increasing the quantum well width, and/or
 2. Increasing the proportion of indium in the quantum well

- By increasing the quantum well width less up-shift of the quantum confined states in the quantum wells is seen, resulting in a shift of the emission wavelength towards the red. This means that less indium is
- 25 required to achieve a given emission wavelength. Thus an optimisation is possible between the well width and indium fraction to achieve the desired emission wavelength whilst avoiding the risk of the quantum well exceeding the critical thickness for relaxation, which would generate defects which reduce the efficiency of light emission. Reducing the indium fraction in the quantum wells also means that the temperature at which the quantum wells are grown is increased reducing the incorporation of impurities
- 30 which again can reduce efficiency.

- As explained above, hexagonal GaN has a polar crystal structure, resulting in a large internal electric field. This internal electric field causes the separation of electrons and holes in the quantum well, reducing the wave function overlap and thus the amount of radiative recombination that occurs. This places a limit on the maximum quantum well thickness that can be used in efficient devices which
- 35 decreases with increasing indium content, ultimately limiting the emission wavelength that can be achieved due to the concomitant energy upshift of confined states in the quantum well. In contrast, the

higher symmetry of cubic GaN is such that there is no internal electric field, thus giving more freedom to increase the quantum well width without inducing these drawbacks. In addition, the smaller native band gap of c-GaN (about 200meV narrower compared to h-GaN) means that the emission wavelength is shifted towards the red at lower indium content, reducing the likelihood of generating defects in the quantum wells.

Cubic GaN phase purity and measurement techniques

Figures 2 – 3 illustrate the difficulty previously associated with forming high-purity cubic GaN. The nano-diffraction map in Figure 2 (original in colour) shows clearly the two phases present, hexagonal and cubic GaN, confirmed by the two distinct peaks in the XRD analysis of Figure 3. In Figure 3, the green, blue and orange lines are the result of fitting curves to the experimental data. Each curve is a Voigt function (a convolution of Gaussian and Lorentz functions) which has been found to replicate the experimental shape of X-ray diffraction peaks. The orange curve is used to improve the fit to the data compared to just two peaks for the main cubic and hex GaN contributions. The orange curve can be interpreted as the volume of highly defective material which does not scatter into the 2 main peaks. This can be thought of as cubic-GaN material with a high density of stacking faults.

Since h-GaN is the thermodynamically stable phase it is difficult to force the GaN to crystallise in the cubic phase and because of the small difference in formation energy of the cubic and hexagonal phases the nucleation and formation of the hexagonal phase is likely to occur on any surface defect during cubic GaN growth, particularly if the (111) plane is exposed. This is because the two phases only differ in their stacking sequence along the [111] direction.

The phase purity is measured by X-ray diffraction, though care should be taken in regard to three key points:

- The reflections chosen to be measured must be sufficiently separated between the cubic and hexagonal phases.
- The phase purity often develops with thickness, and as X-rays have an extinction depth on the order of micrometres it is important that samples of the same thickness are compared.
- The contribution of defective material must be considered, in the case of the cubic phase this presents as stacking faults. This results in a greater intensity at the hexagonal GaN peak and so, the contribution of the defective cubic GaN and the hexagonal GaN must be differentiated.

Figures 4 – 5 show a nano-diffraction map and XRD plot of a GaN sample with 100% cubic phase purity. Figure 5 in particular show that high purity is achievable over large areas as the X-ray signal is collected from several square mm of the sample. Ultimately the whole GaN-based material of the device may exhibit up to 100% cubic phase purity.

The effect of wafer conditions on purity and indium content

Figure 6 shows the near band edge (NBE) peak photoluminescence wavelength across a cubic GaN-based material layer formed epitaxially on a 150mm (001) silicon wafer with an epitaxial 3C-SiC layer formed on the Si substrate. From the image, we can see that the peak wavelength is within the expected range for the cubic GaN phase across the full area of the wafer indicating that cubic GaN phase purity is high. The small variation in near band edge wavelength is considered to be due to small variations in strain of the cubic GaN layer across the wafer.

Holistically it is evident that there is a gradient from 383.3nm to 390.2nm from the edge to the centre of the wafer. From this, it is clear the edges may experience slightly different processing conditions from the centre of the wafer. **Figures 23 and 25** exemplify this more clearly, each shows a corresponding response from different 150mm wafer samples with MQWs grown on them. It is clear here that the wavelength distribution from the quantum wells is not random, in both of these figures, there are two distinct areas on the left and right sides of the wafer that produce longer wavelengths, and there is an area down the middle producing shorter wavelengths. Without wishing to be bound by theory, this is considered to be due to wafer bowing during processing, leading to different local temperatures during the MOCVD process. From the samples of **Figures 23 and 25** it was found that the proportion of indium incorporated into the cubic InGa_N Q-wells is affected by the local temperature conditions. The proportion of indium in turn has an effect on the resulting wavelength.

On the basis of these findings, it was possible for the present inventors to further develop the processes in order to manufacture devices of a small size demonstrating emission at satisfactory wavelength ranges.

Figure 7 shows the Near Band Edge (NBE) emission spectrum taken from about half radius of the n-type cubic GaN layer shown in figure 6. The peak here is 386.2nm, this corresponds to the bandgap energy of cubic GaN, 3.2 eV. This is a lower bandgap and thus a longer wavelength than hexagonal GaN (3.4eV and 364.7nm respectively). Starting at a longer wavelength with pure cubic GaN is advantageous when trying to further increase the wavelength in order to achieve red light emission.

From the starting point of pure cubic GaN with a NBE emission of 386.2nm, the present inventors have found that it is possible to develop suitable combinations of quantum well width and indium content to reach wavelengths in excess of 600nm.

Compatibility with conventional (h-GaN) device processing

Figure 8 displays I/V curves for different Circular Transfer Length Method (C-TLM) gaps for ohmic contacts to n-type cubic GaN processed using a process developed on hexagonal GaN. From this graph, the contact resistivity of the metal-semiconductor junction can be determined. This is done by measuring the resistance between metal contacts at varying distances (or gaps) apart. Here, the I/V characteristics are given for contacts at different distances. As expected, the resistance of the C-TLM structure (slope of the graph) increases (decreases) with increasing size of the gap. Importantly, the I/V

curves remain linear indicating that contacts with a strongly ohmic character are achieved as required in a high performance light emitting device. Specific contact resistance values equivalent to those seen to hex-GaN material were also achieved.

5 Multi-quantum wells and measurements thereof

Figure 9 shows a cross sectional TEM micrograph of a cubic InGaN multiple quantum well (MQW) structure. Here, five quantum wells can be clearly seen, each with a substantially uniform thickness. The use of multiple quantum wells in the active region of the device increases the chance of carrier recombination and consequently LED efficiency. A quantum well is used to confine carriers so that there is a higher chance of an electron and hole combining. Should the carriers leave the quantum well without recombining, less light is produced, and so the provision of further quantum wells further assists in improving efficiency by confining the carriers if they pass through the first quantum well without radiative recombination. Figure 9 shows the implementation of InGaN MQWs in cubic GaN. In the present disclosure, it is considered that a total number of 2 – 5 quantum wells is suitable; however, specialised use cases exist where more may be beneficial.

Measuring the quantum well thickness can be done using HRTEM, or HRSTEM (high resolution scanning transmission electron microscopy). These techniques allow the lattice fringe spacing to be measured and therefore in principle the thickness of the quantum wells can be measured to a precision of about half the thickness of a unit cell (0.225nm in the case of cubic GaN). These techniques give a local measure of the quantum well thickness.

It is known for hexagonal GaN LEDs that the quantum well thickness can be measured from the spacing of the superlattice peaks in X-ray diffraction. This provides a thickness which is averaged over a large area and is often quoted to a precision of 0.1nm. This method can also be applied to cubic GaN LEDs.

25 Full-width at half maximum and peak wavelength

Figure 10 shows the photoluminescence peak from a 10nm wide cubic InGaN quantum well with approximately 10% indium, where λ is the peak wavelength measured as 540nm and $\Delta\lambda$ is the Full-Width at Half Maximum (FWHM). For some use cases, it may be preferred for the FWHM to be low so that substantially all of the visible light emitted coincides with the desired wavelength. If the light source is broad (in terms of the wavelength range emitted) the perception may be that the colour is not clearly defined. This is pertinent when using LEDs for displays as colour accuracy and colour calibration are key functions. Figure 10 shows a FWHM of 125nm, however, it is seen in Figure 17 that this can be reduced to just above 65nm. It is preferable in some embodiments for the FWHM to be less than 50nm.

Figure 17 displays data points for a sample measuring the FWHM and integrated power at different points on the LED surface, and it can be seen the average FWHM lies below 70nm. **Figures 18 and 19** show an optical micrograph and emission spectra respectively of the same device.

In these figures we are using peak wavelength to define the LED emission wavelength, this is taken as the maxima from the emission spectrum. Alternatively, one could use the dominant wavelength to define the LED colour. This is a photometric quantity and so more accurately describes how the colour would be perceived. Both these methods are valid and viable for measurement of output wavelength for the current invention and their measurement will be well known and understood by the skilled person.

Discussion of the quantum well width and efficiency

Figure 11 shows that with increasing well thickness there is an increase in emission wavelength, this is indicated by the blue line. The orange line shows a small corresponding drop in the integrated photoluminescence intensity with increasing emission wavelength.

However, this drop in intensity is small when compared to what is expected for h-GaN Q-wells where due to the internal electric field the intensity would drop to very low levels for Q-well thicknesses above 4nm. This demonstrates that in the case of c-GaN quantum wells the internal fields are removed and useful light emission can be maintained for significantly thicker Q-wells providing an extra degree of freedom in the design of long wavelength high efficiency Q-wells.

microLED structure and growth

Figure 12 shows a schematic example semiconductor structure of the invention, outlining a way in which the layers are arranged. An Si(001) substrate is first provided.

On the Si substrate is grown an epitaxial 3C-SiC(001) layer. This 3C-SiC layer has a relatively small lattice mismatch to cubic-GaN (about 3.4%) and is therefore suitable for subsequent high quality c-GaN growth.

A buffer layer of thickness about 2.5µm thick is then grown. **Figure 20** measures the photoluminescence emission spectra of a 500nm thick cubic GaN layer atop a 1.5µm thick AlGaIn buffer layer. The resulting effect on the NBE spectra of cubic GaN is minimal, the peak wavelength increasing slightly from 386.2 to 388.5nm, which a result of the strain being changed slightly.

An epitaxial n-type GaN-based layer is then formed, followed by the active region and the p-type GaN-based layer. The active region includes at least one quantum well comprising a cubic $\text{In}_x\text{Ga}_{1-x}\text{N}$ -based material, where:

$$x \geq 0.1$$

$$x \leq 0.5$$

Processing conditions are now explained for the manufacture of an exemplary device.

Growth of the cubic GaN layer is initiated on the 3C-SiC/Si substrate using a nitridation process. This involves exposing the substrate surface to a flow of a mixture of ammonia and hydrogen at a reactor pressure of 100 Torr and a temperature of about 960 °C. Nitridation of the surface removes oxide from the SiC surface and populates the surface with N atoms ready to form GaN when Ga is made available.

5

A GaN nucleation layer is then deposited at a reactor pressure of 500 Torr and a temperature in the range 550 °C to 650 °C using trimethylgallium (TMG) and ammonia (NH₃) as gallium and nitrogen sources respectively. The nucleation layer is deposited to a thickness of between 20nm and 40nm to ensure that the SiC surface is completely covered.

10

After deposition of the nucleation layer it is annealed as the temperature of the wafer is raised to the desired temperature for the growth of the cubic-GaN epilayer. This anneal step allows recrystallization of the nucleation layer to improve the crystal quality. The anneal is performed at 100Torr in a flow of NH₃ (and hydrogen) which prevents decomposition of the nucleation layer at higher temperatures and the formation of crystal facets which could nucleate the hexagonal phase at the GaN nucleation layer surface. The temperature is ramped at a rate of about 1 °C/sec to the epilayer growth temperature and then held for about 30seconds to allow the temperature to stabilise.

15

Once the temperature has stabilised at the desired epilayer growth temperature in the range of about 860 to 900 °C, the epilayer growth is carried out at a pressure of 100Torr and a V/III ratio in the range of 40 to 300. The V/III ratio can be adjusted within this range to give the desired layer properties, i.e. suppressing the formation of hex-GaN, controlling the surface morphology of the layer to give a smooth surface and controlling the incorporation of impurities into the layer such as carbon. N-type dopants such as silicon can also be introduced into the layer to give a n-type layer which forms the n-side of the light emitting diode. Typical n-type doping sources are the same as those used in hex-GaN such as silane, disilane or germane.

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Note that it is possible to provide a buffer layer between the SiC layer and the GaN layer, if desired, in order to manage the thermal expansion mismatch between these layers. This buffer layer could consist of an AlN layer or an Al(x)Ga(1-x)N layer where the composition is varied in a stepwise fashion or is continually graded or a combination of a AlN/Al(x)Ga(1-x)N layers.

30

The active region of the device consists of InGa_{0.5}Ga_{0.5}N quantum wells. Due to the formation of highly volatile In-H species, deposition of InGa_{0.5}Ga_{0.5}N is typically performed in an N₂ carrier gas and therefore before the deposition of the quantum wells, the reactor flow is typically switched to N₂ and all H₂ purged from the

35

reactor. InGaN deposition then occurs at a reactor pressure of 300 Torr with NH_3 flow of 9600 Sccm and a temperature of between 600 and 700 °C. A lower temperature results in the incorporation of more indium into the quantum wells with a growth temperature in the region of 620 to 630 °C required (in this exemplary embodiment) to give an emission wavelength of the order of 630nm and growth temperatures
5 in the range of 670 to 680 °C required (in this exemplary embodiment) to give an emission wavelength of the order of 580nm

Following growth of a quantum well, a quantum barrier is grown to help confine the carriers. To grow the quantum barrier the TMI source is turned off so that only Ga is deposited. To prevent the loss of indium
10 from the quantum well at higher temperatures, a thin cap (about 2nm) of GaN is deposited at the growth temperature of the quantum well before pausing growth, by turning off the Ga flow, and ramping the temperature up by about 100 °C. Increasing the temperature of the quantum barrier growth improves the crystal quality of the quantum barrier and reducing the incorporation of impurities which may act as non-radiative defects. A quantum barrier of about 10nm thickness is then grown at the higher temperature.
15 The thickness of the quantum barrier may be changed to affect, and preferably optimise, the efficiency of light emission in Q-wells of different composition and thickness. Growth is then paused and the temperature reduced to allow further quantum wells to be deposited and the process is repeated to give the desired number of quantum wells in the active region of the devices.

20 Following growth of the active region, the carrier gas in the reactor is switched from N_2 to H_2 and a p-type layer is grown to form the p-side of the light emitting diode. P-doping is achieved using a CP_2Mg source similar to that used for p-doping of hex-GaN. This p-layer may include an AlGaIn electron blocking layer to help prevent electrons from escaping the active region.

25 **Figures 13 and 14** show an image and electroluminescence spectrum respectively of a functional biased green cubic GaN LED with a peak wavelength of 520nm and likewise **Figures 15 and 16** show a picture and electroluminescence spectrum respectively of a functional, biased yellow cubic GaN LED with a peak wavelength of 600nm.

30 Efficiency

Figure 21 shows the results of taking a single device and performing a series of micro-photoluminescence internal quantum efficiency (PL-IQE) measurement at multiple points on the device. This measurement assumes that the efficiency is close to 100% at low temperature (approaching zero kelvin) and therefore the PL-IQE is given by the ratio of light intensity emitted at room temperature to that
35 at low temperature. The vertical axis of Figure 21 shows the number of data points (i.e. frequency) with a

specific value of PL-IQE and therefore does not have any units. Here, we see a peak of 10% with some points measuring in excess of 30% at room temperature. PL-IQE gives a measure of the upper limit of performance that could be expected in a full LED device, but does not consider issues such as carrier injection into the Q-wells or the ability of light to escape from the structure once it is generated. Therefore
5 alternative measurements of efficiency could also be used. For example, electro-luminescence (EL-IQE) by its nature does take into account the injection of carriers into the Q-wells, however it is difficult to extract an absolute IQE value unless the light extraction efficiency of the particular device structure used is well known. In this case the external quantum efficiency (EQE) is more easily measurable, and is defined as the average number of photons emitted from the device per electron injected into the device.
10 The EQE value will be lower than both the PL-IQE and EL-IQE measured at the same point. Whilst both IQE and EQE parameters are useful means to measure device efficiency, IQE gives a measure of the performance at the materials level and EQE takes into account the geometry of the light emitting surface in the device which becomes a major contributor to efficiency in microLEDs.

15 Analysis of samples

Figure 22 shows the photoluminescence response from a single point on the wafer investigated in Figures 23 and 24. The key features are the NBE peak at approximately 390nm and the peak from the Q-wells at about 600nm, thus exemplifying a red cubic LED produced on a 150mm silicon wafer. Note that the two very sharp peaks at about 540nm and 810nm are artefacts from the pump laser. **Figure 24**
20 provides the corresponding intensity map to Figure 23, where it can be seen, in line with Figure 11 that longer wavelengths are produced at lower intensity.

Figure 26 shows a similar photoluminescence response to Figure 22, this corresponds to the silicon wafer investigated in Figure 25.

25

The Nomarski images of **Figures 27 and 29** show the surface morphology of their respective samples which consist of a single quantum well designed to emit at longer wavelengths. These pair with the corresponding photoluminescence emission spectra in **Figures 28 and 30** respectively. Figures 27 and 28 pertain to a sample with a quantum well emission at 550nm and Figures 29 and 30 pertain to a sample
30 with a quantum well emission at 605nm. The samples exhibit good photoluminescence.

Figures 31 – 48 show optical micrographs and corresponding electroluminescence emission plots for different exemplary microLED devices. Of these, seven samples have mesa radii of 25µm and two have a mesa radii of 50µm. The peak wavelengths vary in colour from green to red. **Figure 41** shows the
35 microLED of the shortest wavelength but also of the highest quality from this set of figures. The optical images show that its brightness is relatively high, and uniform across the device – whilst the

electroluminescence peak is narrow with little noise. At the time of writing, a long wavelength sample, **Figure 35** for example, is comparatively dimmer. The optical image of this LED shows a speckled surface. Without wishing to be bound by theory, it is considered that in this preliminary result this non-uniformity is due to the challenge of increasing the quantum well width and indium content of the active region. This results in some non-uniformity of the quantum wells, resulting in some areas of slightly lower efficiency. As a result, the active region is not homogeneous, having localised regions emitting shorter wavelengths than that of the electroluminescence peak. This behaviour is quantified in the electroluminescence emission spectrum of **Figure 36**, giving a relatively wide FWHM. **Figures 33 and 34** show an improvement in microLED intensity and quality, this sample having a wavelength peak of 610nm whilst maintaining a relatively narrow FWHM.

Figure 49 shows a plot of raw peak efficiencies for devices with a range of wavelengths.

Relationship between indium content, quantum well width and wavelength

The cubic GaN microLED of this invention has a wavelength that is a result of two key parameters: the indium content in the active region and the quantum well width.

The theoretical variation of wavelength with changing indium content has been plotted for three quantum well widths in **Figure 50**. Each line gives an expected wavelength for a given indium content at that specific quantum well width. As quantum well width is not a discretised value, a better description for the parameter space in which the microLED devices of this invention occupy can be found.

The following empirical equation is proposed:

$$\text{electroluminescence peak wavelength} = xt_{QW}(Ax + B) + C$$

where:

A is a dimensionless number in the range 90-125

B is a dimensionless number in the range 50-95

C is the near band edge (NBE) wavelength of cubic gallium nitride, expressed in nm

t_{QW} is the quantum well width, expressed in nm and in the range 2.5-10nm

x is the indium fraction in the quantum well.

Considering narrower ranges for some of these variables, **Figure 51** shows the plot of Fig. 50 but with a shaded area superimposed, indicating the area bounded by using the following ranges:

A = 90-125

B = 50-95

$t_{QW} = 8\text{nm}$

$x = 0.1 - 0.5$

Figure 52 shows the area bounded when using tighter ranges of variables:

5 $A = 100-115$

$B = 60-85$

$t_{QW} = 8\text{nm}$

$x = 0.1 - 0.5$

10 **Figure 53** shows the area bounded when using even tighter ranges of variables:

$A = 105-110$

$B = 70-75$

$t_{QW} = 8\text{nm}$

$x = 0.1 - 0.5$

15

Figure 54 shows the area bounded when using a 15nm quantum well and the following ranges of variables:

$A = 90-125$

$B = 50-95$

20 $t_{QW} = 10\text{nm}$

$x = 0.1 - 0.5$

25

The purpose of Figures 50-54 is to show the typical combinations of QW thickness and indium content with which it can be expected to be possible to generate red light emission from a cubic GaN-based microLED.

30 The features disclosed in the foregoing description, or in the following claims, or in the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for obtaining the disclosed results, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

35 While the invention has been described in conjunction with the exemplary embodiments described above, many equivalent modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly, the exemplary embodiments of the invention set forth above are considered to

be illustrative and not limiting. Various changes to the described embodiments may be made without departing from the spirit and scope of the invention.

For the avoidance of any doubt, any theoretical explanations provided herein are provided for the purposes of improving the understanding of a reader. The inventors do not wish to be bound by any of these theoretical explanations.

Any section headings used herein are for organizational purposes only and are not to be construed as limiting the subject matter described.

10

Throughout this specification, including the claims which follow, unless the context requires otherwise, the word “comprise” and “include”, and variations such as “comprises”, “comprising”, and “including” will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

15

It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Ranges may be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by the use of the antecedent “about,” it will be understood that the particular value forms another embodiment. The term “about” in relation to a numerical value is optional and means for example +/- 10%.

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References

A number of publications are cited above in order to more fully describe and disclose the invention and the state of the art to which the invention pertains. Full citations for these references are provided below. The entirety of each of these references is incorporated herein.

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International patent application publication number WO 2018/178315 A1

Binks, D.J. *et al.* (2022) ‘Cubic GaN and InGaN/GaN Quantum wells’, *Applied Physics Reviews*, 9(4). doi:10.1063/5.0097558.

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Claims:

1. A light emitting diode comprising:
an n-type cubic GaN-based layer;
5 a p-type cubic GaN-based layer;
an active region formed between the n-type and p-type cubic GaN-based layers;
wherein:
the active region comprises at least one quantum well formed of cubic $\text{In}_x\text{Ga}_{1-x}\text{N}$ -based material
with thickness t_{QW} ;
10 the in-plane area of the active region is not more than $10,000 \mu\text{m}^2$;
the light emitting diode has an electroluminescence peak wavelength in the range 600-750 nm;
and
the thickness t_{QW} and indium content x satisfy the following relationships:
 $t_{\text{QW}} \geq 2.5 \text{ nm}$
15 $t_{\text{QW}} \leq 10 \text{ nm}$
 $x \geq 0.1$
 $x \leq 0.5$
2. The light emitting diode of claim 1, wherein the electroluminescence peak wavelength varies
20 according to the following equation:

$$\text{electroluminescence peak wavelength} = xt_{\text{QW}}(Ax + B) + C$$
where:
A is a dimensionless number in the range 90-125
25 B is a dimensionless number in the range 50-95
C is the near band edge (NBE) wavelength of cubic gallium nitride, expressed in nm.
3. The light emitting diode of any of claim 1 or claim 2 having an external quantum efficiency of at
least 5%.
- 30 4. The light emitting diode of any one of claims 1 to 3 wherein x is in the range 0.3-0.45.
5. The light emitting diode of any one of claims 1 to 4 wherein the active region has a smallest in-
plane dimension of at least $0.1 \mu\text{m}$.
- 35 6. The light emitting diode of any one of claims 1 to 5 wherein the n-type cubic GaN-based layer,
the active region and the p-type cubic GaN-based layer are at least 90% cubic.
7. The light emitting diode of any one of claims 1 to 6 wherein the electroluminescence peak lies in
40 the range of 620 to 650 nm.

8. The light emitting diode of any one of claims 1 to 7 comprising from two to five quantum wells, with cubic GaN-based quantum barriers positioned between adjacent quantum wells.
- 5 9. The light emitting diode of any one of claims 1 to 8 further comprising a substrate comprising:
a (001) oriented 3C-SiC layer;
a cubic GaN-based buffer layer.
- 10 10. The light emitting diode of claim 9 wherein the thickness of the cubic GaN-based buffer layer is at least 2.5 μm .
- 11 11. The light emitting diode of any one of claims 1 to 10 wherein the electroluminescence peak wavelength in the range 600-750 nm has a FWHM of not more than 90 nm.
- 12 12. A light emitting device array comprising at least one pixel itself comprising at least three sub-pixels, being a red sub pixel formed of a cubic GaN-based LED and being according to any one of claims 1-11, a green sub-pixel formed of a GaN-based LED, and a blue sub-pixel formed of a GaN-based LED.
- 13 13. The light emitting device array of claim 12, wherein the height of each sub-pixel is substantially the same.
- 20 14. A method for manufacturing a light emitting diode according to any one of claims 1-11, comprising the steps:
providing a (001) silicon wafer substrate with a (001) 3C-SiC epitaxial layer;
growing a cubic GaN-based epitaxial buffer layer on the (001) 3C-SiC epitaxial layer;
25 epitaxially growing the n-type cubic GaN-based layer;
epitaxially growing the active region on the n-type cubic GaN-based layer;
epitaxially growing the p-type cubic GaN-based layer on the active region.
- 30 15. The method of claim 14 wherein the (001) silicon wafer substrate has a diameter of 100mm or larger.