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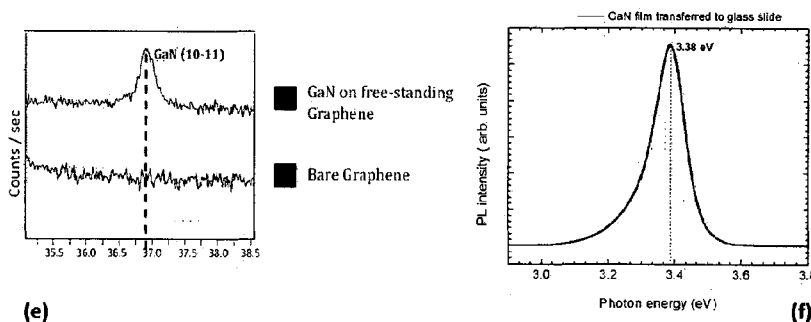
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(54) Title: GROUP III-NITRIDE SEMICONDUCTING MATERIAL AND A METHOD OF MANUFACTURING THE SAME



(57) Abstract: Group III-nitride semiconducting materials comprising a graphene based layer having thereon at least one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and at least one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B) N on said nitride nucleation/buffer layer, in orientations selected from polar, non-polar and semi-polar with or without a suitable underlying substrate, and planar free-standing said Group III-nitride semiconducting material that is advantageously transferable to a wide variety of substrates selected from glass or flexible plastic substrates and adapted for the fabrication of various optoelectronic devices including LEDs, lasers, transistors.

**TITLE: GROUP III-NITRIDE SEMICONDUCTING MATERIAL AND A METHOD OF MANUFACTURING THE SAME****FIELD OF INVENTION**

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The present invention relates to Group III-nitride semiconducting materials comprising a graphene based layer having thereon at least one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B) N on said nitride nucleation/buffer layer, in orientations selected from polar, non-polar and semi-polar with or without a suitable underlying substrate. The said Group III-nitride semiconducting film in the semiconducting material of the present invention comprises one or more layers of dissimilar compositions of the (Al, Ga, In, B) N alloy family selected from at least one or more of: binary GaN, AlN, InN compound semiconductors; ternary alloys of AlGaIn, AlInN, InGaIn; or quaternary alloys of AlGaInN and the like, in said film. The present invention more particularly relates to planar, free-standing said Group III-nitride semiconducting material comprising graphene as the selective intermediate layer having deposited thereon at least one Group III-nitride semiconducting film in semi-polar orientations such as (10-11), (11-22), (10-13), wherein said graphene as the selective intermediate layer having at least one nitride nucleation/ buffer layer allows the growth of said Group III nitride semiconducting film in said semi-polar orientations. Also the present invention relates to an improved method of manufacturing said planar, group III-nitride semiconducting material scalable to large area preferably in semi-polar orientation, and more preferably, also relates to a method of providing free standing layers/ membrane of said group-III nitride semiconducting material that is advantageously transferable to a wide variety of substrates selected from glass or flexible plastic substrates and adapted for the fabrication of various optoelectronic devices including LEDs, lasers, transistors.

30 **BACKGROUND ART**

Gallium nitride and related ternary and quaternary alloys are well-established as important materials for light emitting diodes and lasers in the UV/visible region. In general, the most stable crystal structure of group III nitrides is the hexagonal wurtzite form. Further, most single crystal thin films of the group III nitrides are grown on the basal plane, i.e. the c-plane or (0001) oriented plane. In this orientation, the alternating layers of Gallium and Nitrogen atoms lead to a spontaneous polarization that induces an

internal electric field. In addition, most nitrides are grown on sapphire, in which lattice mismatch results in strain, which further leads to piezoelectric polarization.

5 Such internal electric fields are often deleterious for optoelectronic devices as they reduce the recombination efficiency of electrons and holes and also make it difficult to push towards the optical emission of lasers and LEDs to longer wavelengths. The problem of polarization is most acute on standard basal plane (0001) of the wurtzite crystal structure.

10 There are other crystal planes perpendicular to the (0001) plane which have equal number of group III and group V atoms, and hence form "non-polar" surfaces. Materials grown on the so-called a-plane [11-20] and m-plane [1-100] directions thus have no net polarization field in the growth direction. Unfortunately, inspite of worldwide efforts on synthesis of non-polar nitrides, there are still difficulties related to obtaining smooth  
15 layers as well as there exist problems with indium incorporation in non-polar oriented epilayers.

Furthermore, there exist other planes of wurtzite structure which are at an angle to the basal plane and offer not non-zero, but greatly reduced polarization fields compared to  
20 the c-plane. (Such "semi-polar" planes have both two non-zero h, i, or k Miller indices, and a non-zero l Miller index – examples being {11-22}, {10-11}, {10-13} etc.). It is well known from recent experimental studies that these planes are advantageous from the growth standpoint as they offer increased indium incorporation for InGaN quantum wells as well as are smoother and more homogenous layers compared to growth on non-  
25 polar orientations. Such semi-polar layers have been used to demonstrate green LEDs and lasers.

Polarization-related issues are a major cause of concern in the performance of these devices, especially in the widely used crystal orientation—the standard basal plane  
30 (0001) of the wurtzite crystal structure. Recent experimental evidence suggests that the use of "semi-polar" planes (wurtzite crystal planes such as {11-22}, {10-11}, {10-13} etc.) are advantageous for optoelectronic devices, and such semi-polar layers have been used to demonstrate the best green LEDs and lasers. Unfortunately there is no easy way to grow semi-polar nitride layers on sapphire, even using misoriented substrates.

35 Till date there is no facile way to produce large area (tens to hundreds of cm<sup>2</sup>) semi-polar nitride films that would be useful for large-scale industrial applications. Most

currently available semi-polar films utilize quasi-bulk semi-polar GaN substrates, which are made by cutting boules of HVPE grown GaN nitrides along semi-polar directions resulting in substrates which are typically only a few mm across and limited by the thickness of the starting HVPE material.

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US Patents including US 7,687,293, US 7,575,947, US 7,790,584 and US 7,704,324 disclose methods for growing a semi-polar nitride semiconductor thin film on a substrate, all of which require either a complicated multi-step etch, or re-growth processes, or achieve the semi-polar surface only in certain regions of the wafer, or require miscut /misoriented substrates.

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Graphene has been a material of contemporary research interest as it can serve as a transparent conducting electrode for use in various optoelectronic devices. However the growth of III-Nitride materials such as GaN on graphene has not received much attention possibly due to the chemical inertness of the graphene surface. A recent publication by Chung et al. (Science, 310, 655, 2010) claims that GaN nucleation does not occur on the basal plane of pristine graphene, and some GaN islands grow on roughened graphene surfaces subjected to Oxygen-plasma treatment. They say that even the typical two-temperature growth process using a low-temperature GaN buffer layer does not improve the film properties. Hence they use zinc oxide as an intermediate layer for GaN growth. Thus there is still no clear method for achieving the growth of planar large-area films of III-Nitride semiconductors on graphene.

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As apparent from the above, there is therefore a longfelt need in the art to overcome the deficiencies of the prior art methods to develop planar group III-nitride semiconducting material with semi-polar orientations and a method for growing said material on substrates which would not need any special miscut / misoriented substrates, which method would be scalable, useful for large scale industrial applications and would be industrially facile in not involving a multi-step process such as not requiring plasma processing and re-growth thereafter. Also there is a strong need in the art to explore methodologies that would be advantageous in simultaneously providing for free standing layers/ membrane of said group III-nitride semiconducting material transferable to a wide variety of substrates for the purpose of fabrication of wide range of optoelectronic devices.

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#### **OBJECTS OF THE INVENTION**

It is thus a primary object of the present invention to provide for planar group III-nitride semiconducting (Al, Ga, In, B)N material with one or more orientations selected from

polar, non-polar and semi-polar, preferably with semi-polar orientations such as (10-11), (11-22), (10-13) as a single phase material and a simple yet improved method for manufacturing the same.

It is another object of the present invention to provide for free standing layers/membrane of said group III-nitride semiconducting (Al, Ga, In, B)N material to enable fabrication of wide range of optoelectronic devices including LEDs, lasers, transistors involving said free-standing layers/ membrane and a method to achieve the same involving the steps of lifting off the group III-nitride material from the substrate on which it is deposited so as to transfer it to another substrate.

It is another object of the present invention to provide for a method of fabricating said group III-nitride semiconducting material under appropriate growth conditions by depositing a selective intermediate layer on a substrate prior to the growth of the nitride semiconducting layer to enable growth of said material in said semipolar orientations.

It is yet another object of the invention to provide a method of growing planar, group III-nitride semiconducting (Al,In,Ga,B)N material that would be easily scalable to large area and useful for large scale industrial applications.

It is yet another object of the present invention to provide for a method of manufacturing nitride semiconducting (Al,In,Ga,B)N material that would not require specially miscut/ mis-oriented substrates.

#### **SUMMARY OF THE INVENTION**

Thus according to the basic aspect of the present invention there is provided a Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N on said nitride nucleation /buffer layer.

It is by way of the present invention that it has been possible to provide at least one nitride nucleation/buffer layer adapted for conformal coverage of entire graphene based layer and thereon providing for atleast one group III-nitride semiconducting film selected

from alloy family of (Al,Ga,In,B)N on said nitride nucleation /buffer layer, that enabled the provision of the much desired single phase semiconducting material and preferably even in semi-polar orientations.

5 The single phase semiconducting material of the present invention which involves a graphene based layer is also advantageous in that the same is easily scalable to large area and also advantageously transferable to a wide variety of substrates selected from glass or flexible plastic substrates adapted as free standing layers/ membrane of said Group III-nitride semiconducting material favouring fabrication of various optoelectronic  
10 devices.

According to another preferred aspect of the present invention there is provided said Group III-nitride semiconducting material wherein said group III-nitride semiconducting films of (Al, Ga, In, B) N comprise at least one or more layers of dissimilar compositions  
15 within the alloy family of (Al,Ga,In,B)N.

According to yet another preferred aspect of the present invention there is provided said Group III-nitride semiconducting material wherein graphene based group III-nitride semiconducting film is planar with one or more orientations selected from polar, non-  
20 polar and semi-polar and selected from the group comprising of GaN, AlN, InN, AlGaN, AlInN, InGaN and AlGaInN.

According to another preferred aspect of the present invention there is provided said Group III-nitride semiconducting material wherein said graphene based group III-nitride  
25 semiconducting films comprise one or more layers of dissimilar compositions of the (Al, Ga, In, B) N alloy family selected from at least one or more of: GaN, AlN, InN alloys; ternary alloys of AlGaN, AlInN, InGaN; or quaternary alloys of AlGaInN and the like, in said film.

30 According to another aspect of the present invention there is provided Group III-nitride semiconducting material wherein said graphene based group III-nitride semiconducting films comprise free standing graphene based films with one or more orientations selected from polar, non-polar and semi-polar preferably with semi-polar orientations selected from (10-11), (11-22), (10-13) as a single phase material.  
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According to another preferred aspect of the present invention there is provided said Group III-nitride semiconducting material wherein said graphene based group III-nitride

semiconducting free standing films shaped and configured for variety of applications.

5 Said graphene based group III-nitride semiconducting films are provided on suitable substrates include rigid substrates preferably including glass or transparent conducting oxide (TCO) coated glass, and/or flexible substrates preferably including plastics or metal foils.

10 More preferably, said Group III-nitride semiconducting material wherein said nitride nucleation/buffer layer adapted for conformal coverage of entire graphene surface comprise is an alloy selected from combinations of alloy family (Al, In, Ga)N preferably AlN.

15 According to another aspect of the present invention there is provided said Group III-nitride semiconducting material comprising said graphene based group III-nitride semiconducting films on suitable substrates including sapphire, patterned sapphire, silicon, silicon oxide /dioxide coated silicon, silicon nitride coated silicon, silicon carbide and glass.

20 According to another aspect of the present invention there is provided said graphene based group III-nitride semiconducting films adapted as free standing films on releasable sacrificial substrate layers including silicon oxide/dioxide, silicon nitride, spin-on-glass, polyimides.

25 According to another aspect of the present invention there is provided said graphene Group III-nitride semiconducting films scalable to a large area from 10s to about 100s of cm<sup>2</sup> adapted for various optoelectronic devices.

30 According to another aspect of the present invention there is provided a Group III-nitride semiconducting material comprising of graphene based layer having thereon at least one AlN nucleation /buffer layer having conformal coverage of entire graphene surface and at least one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N on said nitride nucleation /buffer layer with semi-polar orientations selected from (10-11), (11-22), (10-13).

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According to another aspect of the present invention there is provided a method of manufacture of Group III-nitride semiconducting material comprising

- a) providing a graphene based layer on a substrate;
- b) providing said nitride nucleation /buffer layer having conformal coverage on entire graphene based layer; and
- c) providing thereon said nucleation /buffer layer, atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom graphene based group III nitride semiconducting films of desired thickness.

According to another preferred aspect of the present invention there is provided a method of manufacture of Group III-nitride semiconducting material comprising

- a) providing a graphene based layer on a substrate;
- b) providing said AlN nucleation /buffer layer having conformal coverage on entire graphene based layer; and
- c) providing thereon said AlN nucleation /buffer layer having conformal coverage, atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom graphene based group III nitride semiconducting films of desired thickness.

The single phase semiconducting material of the present invention could avoid the limitations of achieving graphene based semiconducting materials with planar large area films by the above control of process parameters whereby even in the absence of specially miscut or mis-oriented sapphire or spinel substrates allows attainment of said Group III-nitride semiconducting material as a single phase material of high material quality with preferred semi-polar orientations that is advantageously both scalable to large area and also transferable to a wide variety of substrates adapted as free standing layers/ membrane of planar large-area films of said Group III-nitride semiconductors.

Preferably, said nitride nucleation /buffer layer is grown on said graphene layer such as to achieve said conformal coverage on entire graphene based layer followed by growing thereon said nitride nucleation /buffer layer the said nitride semiconducting film involving a semiconductor deposition system and following one or more of techniques selected from metal organic chemical vapor deposition (MOCVD), metal organic vapour phase epitaxy (MOVPE), solid or gas source molecular beam epitaxy (MBE), and hydride vapor phase epitaxy (HVPE).

More preferably, said nitride semiconducting film is grown in one or more orientations selected from polar, non-polar and semi-polar.

According to another aspect of the present invention said step (b) of providing a nucleation /buffer layer having conformal coverage on entire graphene based layer comprises the steps of

- 5 (i) surface conditioning of the graphene based layer on the substrate followed by thermal cleaning in the temperature range of 900°C to 1100°C for 3 to 10 min. followed by cooling;
- (ii) growing stagewise said nitride nucleation /buffer layer involving required metalorganic and hydride precursors for nucleation of desired thickness under required system pressure and temperature.

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According to another preferred aspect of the present invention said step of providing AlN as nucleation /buffer layer comprises growing said nucleation /buffer layer involving precursors for nucleation involving low pressure in the range of 20 to 100 Torr following stepwise growth preferably involving either (A) two stage growth comprising (i) following

15 a first stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 700 to 800°C followed by (ii) second stage growth for thickness in the range of 25 to 40 nm at temperature in the range of 1000 to 1100 °C or (B) three stage growth (i) following a first stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 600 to 700 °C (ii) second stage growth for thickness in the

20 range of 10 to 20 nm at temperature in the range of 800 to 950 °C and (iii) third stage growth for thickness in the range of 20 to 30 nm at temperature in the range of 1000 to 1100 °C .

25 According to another aspect of the present invention said step (c) of providing thereon said nitride nucleation /buffer layer, the group III nitride semiconducting film comprises the steps of providing required metalorganic and hydride precursors in the pressure ranging from 20 to 760 Torr, temperature ranging from 530 to 1100 °C, depending on the particular III-Nitride film deposited.

30 According to another preferred aspect of the present invention there is provided said method for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material the said atleast one nitride nucleation /buffer layer is grown in said semipolar orientation (10-11) involving precursors for nucleation and growth in the preferred temperature range of 600 to 1100 °C and pressure in the range of 20 to

35 100Torr and with selective V/III ratio in the range of 3500 to 10000.

According to yet another aspect of the present invention wherein for providing a preferred semipolar orientation (10-11) of Group III-nitride semiconducting material, said AlN as nucleation /buffer layer is grown in said semipolar orientation (10-11) involving precursors for nucleation and growth involving trimethylaluminium, ammonia  
5 and hydrogen carrier gas in the preferred temperature range of 600 to 1100 °C preferably about 1000 °C and pressure in the range of 20 to 100 Torr, preferably 50 Torr and with selective V/III ratio in the range of 2500 to 10000 preferably above 3500.

According to yet another preferred aspect of the present invention wherein for providing  
10 preferred semipolar orientation (10-11) of GaN semiconducting film provided thereon said nitride nucleation /buffer layer comprises growing the GaN film involving trimethylgallium, ammonia and hydrogen carrier gas, at 50 to 200 Torr preferably 50 Torr reactor pressure at temperature 1000 to 1100°C preferably of 1040°C to thereby obtain semi-polar oriented said GaN group III nitride semiconducting film as a single  
15 phase material.

According to another preferred aspect of the present invention for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material wherein providing thereon said AlN nitride nucleation /buffer layer, preferably AlGa<sub>N</sub> as the group  
20 III nitride semiconducting film comprises growing said Group III-nitride film involving selective precursor involving trimethylgallium, trimethylaluminium and ammonia and hydrogen carrier gas, at 50 to 100 Torr preferably 50 Torr reactor pressure at temperature 1000 to 1100°C preferably of 1040°C to thereby obtain semi-polar oriented said group III nitride semiconducting film comprising AlGa<sub>N</sub> semi-polar (10-11) layer  
25 adapted as a single phase material.

According to another preferred aspect of the present invention for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material wherein providing thereon said AlN nitride nucleation /buffer layer, InN or InGa<sub>N</sub> or as the group  
30 III nitride semiconducting film comprises growing the Group III-nitride film involving selective precursor involving trimethylindium, trimethylgallium, and ammonia and nitrogen carrier gas, at 200 to 500 Torr reactor pressure at temperature 530 to 800°C to thereby obtain semi-polar oriented said group III nitride semiconducting film comprising InN semi-polar (10-11) layer or InGa<sub>N</sub> semi-polar (10-11) layer adapted as a single  
35 phase material.

According to yet another preferred aspect of the method of the present invention said

substrate is selected from a group comprising of Sapphire, patterned Sapphire, Silicon, Silicon Oxide/Dioxide coated Silicon, Silicon Nitride coated Silicon, Silicon Carbide and Glass also comprising releasable sacrificial substrate layers including silicon oxide/dioxide, silicon nitride, spin-on-glass, polyimides.

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Preferably, said substrate is surface conditioned prior to deposition of said nitride semiconducting film by exposure to oxygen plasma after which thermal cleaning of the substrate is preferably achieved by heating under hydrogen flow just prior to growth in the semiconductor deposition system.

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According to another aspect of the present invention there is provided a method comprising obtaining free standing graphene based group III nitride semiconducting films comprising

a) providing a graphene based layer on a sacrificial substrate;

15 b) providing said nitride nucleation /buffer layer having conformal coverage on entire graphene based layer;

c) providing thereon said nucleation /buffer layer having conformal coverage, at least one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom graphene based group III nitride semiconducting films of desired

20 thickness; and d) removing the sacrificial layer to thereby obtain free standing Group III-nitride semiconducting material.

According to another aspect of the present invention there is provided a method comprising obtaining free standing graphene based group III nitride semiconducting  
25 films wherein said sacrificial substrate is selected from silicon oxide/ dioxide, silicon nitride, spin-on-glass, polyimides which is removed preferably by chemical etching of the said sacrificial layer, e.g. the silicon dioxide layer below said graphene layer is etched using HF/buffered HF.

30 According to another aspect of the present invention there is provided an optoelectronic device comprising Group III-nitride semiconducting material comprising of graphene based layer having thereon at least one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and at least one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N on said nitride nucleation  
35 /buffer layer with or without a suitable substrate.

According to yet another aspect of the present invention there is provided a

semiconducting material adapted for facilitating epitaxial growth of semiconducting films as epilayer thereon comprising of graphene based layer and atleast one nitride nucleation /buffer layer comprising an alloy selected from combinations of alloy family (Al, In, Ga)N having conformal coverage of entire graphene surface with or without a suitable substrate.

The embodiments herein and the various features and advantageous details thereof are explained more fully with reference to the non-limiting embodiments that are illustrated in the accompanying figures & tables and detailed in the following description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

## 15 BRIEF DESCRIPTION OF FIGURES

**Fig. 1:** depicts scanning electron microscope image showing conformal coverage of entire surface with AlN buffer layer on graphene;

**Fig. 2 (a):** scanning electron microscope image showing conformal coverage of entire surface with GaN deposited on top of AlN nucleation and buffer layer on Graphene; **2(b)** depicts scanning electron microscope image showing the absence of conformal growth of GaN on the entire surface due to its deposition directly on Graphene;

**Fig. 3:** depicts X-ray diffraction (XRD) profiles of the  $\omega$ -2 $\theta$  scan for on-axis reflections for AlN layers grown on graphene at (a) different substrate temperatures and (b) different V/III ratios;

**Fig. 4:** depicts X-ray diffraction (XRD) profiles of the  $\omega$ -2 $\theta$  scan for on-axis reflections showing AlN buffer layer and GaN semi-polar layer (10-11) grown on graphene;

**Fig. 5:** depicts room temperature photoluminescence emission spectra from the semi-polar (10-11) oriented GaN and AlGaIn layers showing high material quality;

**Fig. 6:** depicts X-ray diffraction (XRD) profiles of the  $\omega$ -2 $\theta$  scan for on-axis reflections showing patterns of GaN on AlN on graphene grown under different conditions showing mixed phases at low temperature;

**Fig. 7:** depicts X-ray diffraction (XRD) profiles of the  $\omega$ -2 $\theta$  scan for on-axis reflections of AlGaIn alloy samples of varying aluminium content

**Fig. 8(a)** depicts a process of lift off of free standing GaN layer, after etching the underlying silicon dioxide layer in buffered HF (**Fig.8 b**), the nitride layer floats up on to the surface (**Fig. 8 c**), **Fig. 8 (d)** depicts free-standing GaN layer transferred to a glass slide, and **Fig. 8 (e)** is a x-ray diffraction pattern of the free-standing GaN showing a semi-polar orientation (10-11). **Fig 8 (f)** shows room temperature photoluminescence from the free-standing GaN layer, pointing to the high material quality.

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## DETAILED DESCRIPTION OF THE INVENTION

As discussed hereinbefore, the present invention provides for Group III-nitride semiconducting material comprising graphene based layer having thereon atleast one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and at least one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N on said nitride nucleation /buffer layer, in orientations selected from polar, non-polar and semi-polar with or without a suitable substrate. The said Group III-nitride semiconducting film of the semiconducting material of the present invention comprises one or more layers of dissimilar compositions of the (Al, Ga, In, B) N alloy family selected from at least one or more of: GaN, AlN, InN alloys; ternary alloys of AlGaIn, AlInN, InGaIn; or quaternary alloys of AlGaInN and the like.

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More particularly, the present invention provides for planar free standing semiconducting material scalable to large area and advantageously transferable to a wide variety of substrates selected from glass or flexible plastic substrates thereby favouring fabrication of various optoelectronic devices including LEDs, lasers, transistors wherein said III-nitride semiconducting film preferably involves semi-polar orientation such as (10-11), (11-22), (10-13).

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In an embodiment, the present invention relates to a method of growing planar group III-nitride semiconducting film (Al,Ga,In,B)N on a substrate comprising steps of:

- a) deposition of graphene layer on the substrate; and
- b) deposition of a conformal nitride semiconducting film on the graphene layer adapted for facilitating epitaxial growth of semiconducting films as epilayer thereon.

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The nitride semiconducting film grown by the present method can be deposited in one or

more of orientations selected from polar, non-polar and semi-polar orientations. By appropriate choice of growth conditions semi-polar orientations such as (10-11), (11-22), (10-13) etc. can be obtained.

5 In another embodiment, the planar group III nitride semiconducting film that is grown may contain one or more layers of dissimilar compositions of the (Al,Ga,In,B)N alloy family. For example, films which can be grown by the present method can be one or more of GaN, AlN, InN; ternary alloys like AlGaN, AlInN, InGaN; or quaternary alloys like AlGaInN and the like.

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In an embodiment, the planar group III nitride semiconducting film can be grown using one or more techniques selected from metal organic chemical vapor deposition (MOCVD), metalorganic vapour phase epitaxy (MOVPE), solid and gas source molecular beam epitaxy (MBE), or hydride vapor phase epitaxy (HVPE).

15

In an embodiment of the present invention, the group III-nitride semiconducting film is grown in a semi-polar orientation which is selected from (10-11), (10-13) and (11-22).

20 In an embodiment, semi-polar group III-nitride semiconducting film can be grown on substrates such as Silicon, Sapphire, Silicon Carbide, or Silicon-dioxide/Silicon-nitride coated Silicon substrates using a graphene interlayer. The present method does not require specially miscut or mis-oriented sapphire or spinel substrates.

25 Large area graphene layers used in the present invention can be synthesized using standard Chemical Vapor Deposition (CVD) techniques as disclosed in the literature, for example, through deposition by cracking of methane at high temperature on copper (or nickel) foils, followed by etching and lift-off. (See, for example, Mark Borysiak, "Graphene Synthesis by CVD on Copper Substrates, The 2009 NNIN REU Research Accomplishments, p. 71 to 74 and Matthew O'Brien et al, "CVD Synthesis and  
30 Characterization of Graphene Thin Films", Army Research Laboratory, 2010, p. 1 to 15, <http://www.arl.army.mil/arlreports/2010/ARL-TR-5047.pdf>, and for synthesis on nickel, see for example, K-S. Kim, et al, *Nature* 457, 706-710 (2009).

35 The invention and its advantages are explained hereunder in greater detail in relation to the following non-limiting exemplary illustrations:

**Example I**

5 In accordance with an aspect of the present invention, surface conditioning of the graphene layer prior to deposition of nitride layer was done by exposure to oxygen plasma.

10 Thereafter, the wafer was loaded into an MOVPE reactor and heated under hydrogen flow and thermally cleaned, typically at 1040°C for 5 min before cooling down for deposition of the nucleation or buffer layer.

**Example-II**

15 Under this example the manufacture of Gr. III nitride-semiconducting film involving the graphene based layer following direct deposition of GaN on graphene and with deposition of GaN after conformal coverage of the graphene with nucleation/buffer layer was studied.

20 As a preferred embodiment, the nitride nucleation or buffer layer used was AlN, which was grown conformally as detailed below on the graphene layer (Fig. 1), hence permitting the growth of smooth layers of GaN on top of it (Fig 2a), whereas direct deposition of GaN on the graphene layer (at 1040 °C 50 Torr) results in isolated island growth (Fig. 2b).

25 The process for generating the conformal coverage of the nucleation layer on the graphene followed was as hereunder:

30 An aluminium nitride nucleation or buffer layer was deposited on the graphene layer under appropriate reactor pressure and temperature. In one embodiment, the AlN nucleation layer was grown at a low reactor pressure, for example, 50 Torr, and either as a two step growth – for example, low temperature nucleation step of 15 nm at 600°C, followed by a high temperature grown layer 35 nm at 1040°C, or as a 3-step growth with a low temperature nucleation step of 15 nm at 600°C, followed by 15 nm growth at 900°C, and a high temperature grown buffer layer 35 nm at 1040°C.

35 The reactor temperature was further ramped to an appropriate temperature for growth of desired group III-nitride semiconducting epilayer. The reactor temperature, ranged from 1040°C for GaN to 530°C for InN.

**Example III**

5 Under this example, in accordance with the present invention, the desired group III-nitride semiconducting epilayer was grown on top of an AlN buffer layer by admitting the appropriate metalorganic and hydride precursors at a specific pressure, temperature, V/III ratio, and growth rate to favour a preferential surface orientation of the epilayer. It was noted that typically high temperature and low pressure conditions favored the  
10 growth of semi-polar oriented layers while low temperature and high pressure conditions lead to mixed phases with polar and semi-polar oriented domains.

**Example IV**

15 Under this example, AlN layers were grown using trimethylaluminium and ammonia and hydrogen carrier gas, at growth temperatures ranging from 800°C to 1100°C and V/III ratios from 500 to 5000. Fig. 3 (a) shows the X-ray diffraction (XRD) of the  $\omega$ -2 $\theta$  scan for on-axis reflections for a series of AlN layers grown at different growth temperatures in the range 900 to 1040°C keeping other parameters fixed. From the accompanying  
20 figure it can be seen at lower temperatures mixed phases are obtained, as the temperature increases the intensity of the (0002) peak drops, and reached a minimum at an optimum temperature of 1000°C. Fig. 3(b) shows a series of AlN layers growth at different V/III ratios from 500 to 4500 keeping other parameters fixed. From the figure it can be seen that for growth at low V/III ratio other parasitic phases such as the (0002),  
25 (10-12) and (11-20) are seen. These phases reduce on increasing the V/III ratio, and almost single phase (10-11) semipolar AlN is obtained at V/III ratios above 3500.

**Example V**

In accordance with a preferred aspect of the invention, under this example, GaN and  
30 AlGaIn layers, were grown using trimethylgallium, trimethylaluminium and ammonia and hydrogen carrier gas, growth at 1040°C and 50 Torr reactor pressure leading to layers with a preferential (10-11) orientation (Fig. 4) Fig. 4 shows the X-ray diffraction (XRD) profile of the  $\omega$ -2 $\theta$  scan for on-axis reflections showing AlN buffer layer, GaN semi-polar (10-11) layer and AlGaIn semi-polar (10-11) layer grown on graphene. A single phase  
35 material was thus obtained. Fig. 5 shows the room temperature photoluminescence from these GaN and AlGaIn layers pointing to the high quality of the material.

Growth at 900°C and 200 Torr reactor pressure lead to layers with mixed (10-11) and (0002) orientation (Fig. 6). Fig. 6 shows the X-ray diffraction (XRD) profile of the  $\omega$ -2 $\theta$  scan for on-axis reflections showing patterns of GaN on AlN on graphene grown under different conditions showing mixed phases at low temperature.

5

By varying the relative amounts of trimethylaluminium and trimethylgallium supplied during growth it was possible to adjust the composition of the AlGaN alloy layer to any desired aluminium mole fraction, as shown in Fig. 7 by the typical X-ray diffraction (XRD) profiles of the  $\omega$ -2 $\theta$  scan for on-axis reflections for 4 samples covering the range of Al content from 0 to 100%.

10

InN and In-containing alloys were grown in a similar manner as described herein, but by using nitrogen carrier gas instead of hydrogen.

15 After a group III nitride semiconducting layer of a desired thickness was grown, the supply of reagents was switched off and the reactor cooled to room temperature and the sample removed.

The planar group III nitride films obtained by the present method are found to be advantageously of a large area, limited only by the size of the graphene layer transferred onto the substrate. Since CVD graphene can be grown over large areas (10s to 100s of cm<sup>2</sup>), semi-polar nitride films of large area can thus be obtained by the method of the present invention.

## 25 **Example VI**

In accordance with yet another aspect of the invention, under this example, the graphene layer was transferred to a silicon dioxide or silicon nitride coated substrate (wafer). The silicon dioxide/nitride served as a sacrificial layer in a process for the fabrication of free standing semiconductor layers.

30

In a further embodiment, the method of the present invention provides for fabrication of free-standing layers of the semi-polar nitride semiconductor film. In another preferred embodiment of the present invention, the free-standing nitride film was obtained by chemical etching of the silicon oxide layer below the graphene layer by using HF/buffered HF etchants. This separated the nitride layer on the graphene from the substrate and releases the nitride layer as a free standing membrane, which was then transferred to other materials, such as glass or flexible plastic substrates. (Fig. 8)

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The group III nitride semiconducting material manufactured by the method of the present invention can thus be used advantageously as substrates for a range of optoelectronic device applications such as LEDs, lasers, transistors and the like.

5

**Example VII**

A device preferably an optoelectronic device was fabricated comprising Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N on said nitride nucleation /buffer layer with or without a suitable substrate.

It is thus possible by way of the present invention to provide for Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N on said nitride nucleation /buffer layer with orientations selected from polar, non-polar and semi-polar comprises one or more layers of dissimilar compositions of the (Al, Ga, In, B) N alloy family selected from the group comprising at least one or more of GaN, AlN, InN, AlGaN, AlInN, InGaN or AlGaInN.:GaN, AlN, InN alloys.

Importantly, the present invention provides for planar free standing layers/ membrane of said Group III-nitride semiconducting material scalable to large area and advantageously transferable to a wide variety of substrates selected from glass or flexible plastic substrates thereby favouring fabrication of various optoelectronic devices including LEDs, lasers, transistors, wherein said graphene based group III-nitride semiconducting film involves semi-polar orientation selected from (10-11), (11-22), (10-13) as a single phase material.

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**We Claim:**

1. Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N on said nitride nucleation /buffer layer.  
5
2. Group III-nitride semiconducting material as claimed in claim 1 wherein said group III-nitride semiconducting films of (Al, Ga, In, B) N comprise at least one or more layers of dissimilar compositions within the alloy family of (Al,Ga,In,B)N.  
10
3. Group III-nitride semiconducting material as claimed in anyone of claims 1 or 2 wherein graphene based group III-nitride semiconducting film is planar with one or more orientations selected from polar, non-polar and semi-polar and selected from the group comprising of GaN, AlN, InN, AlGaN, AlInN, InGaN and AlGaInN.  
15
4. Group III-nitride semiconducting material as claimed in anyone of the preceding claims wherein said graphene based group III-nitride semiconducting films comprise one or more layers of dissimilar compositions of the (Al, Ga, In, B) N alloy family selected from at least one or more of: GaN, AlN, InN alloys; ternary alloys of AlGaN, AlInN, InGaN; or quaternary alloys of AlGaInN and the like, in said film.  
20
5. Group III-nitride semiconducting material as claimed in anyone of the preceding claims wherein said graphene based group III-nitride semiconducting films comprise free standing graphene based films with one or more orientations selected from polar, non-polar and semi-polar preferably with semi-polar orientations selected from (10-11), (11-22), (10-13) as a single phase material.  
25
6. Group III-nitride semiconducting material as claimed in anyone of the preceding claims comprising said graphene based group III-nitride semiconducting free standing films shaped and configured for variety of applications.  
30
7. Group III-nitride semiconducting material as claimed in anyone of the preceding claims comprising said graphene based group III-nitride semiconducting films on suitable substrates including rigid substrates preferably including glass, transparent conducting oxide (TCO) coated glass and/or flexible substrates preferably including plastics, metal foils.  
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8. Group III-nitride semiconducting material as claimed in any of the preceding claims wherein said nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface comprise an alloy selected from combinations of alloy family (Al, In, Ga)N preferably AlN.
9. Group III-nitride semiconducting material as claimed in any of the preceding claims comprising said graphene based group III-nitride semiconducting films on suitable substrates including sapphire, patterned sapphire, silicon, silicon oxide /dioxide coated silicon, silicon nitride coated silicon, silicon carbide and glass.
10. Group III-nitride semiconducting material as claimed in any of the preceding claims comprising graphene based group III-nitride semiconducting films adapted as free standing films on releasable sacrificial substrate layers including silicon oxide/dioxide, silicon nitride, spin-on-glass, polyimides.
11. Group III-nitride semiconducting material as claimed in any of the preceding claims comprising graphene based group III-nitride semiconducting films scalable to a large area including from 10s to about 100s of cm<sup>2</sup> adapted for various optoelectronic devices.
12. Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one AlN nucleation /buffer layer having conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N on said nitride nucleation /buffer layer with semi-polar orientations selected from (10-11), (11-22), (10-13).
13. A method of manufacture of Group III-nitride semiconducting material as claimed in anyone of claims 1 to 12 comprising
- a) providing a graphene based layer on a substrate;
  - b) providing said nitride nucleation /buffer layer having conformal coverage on entire graphene based layer; and
  - c) providing thereon said nucleation/buffer layer, atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom graphene based group III nitride semiconducting films of desired thickness.
14. A method of manufacture of Group III-nitride semiconducting material as claimed in claim 13 comprising

- a) providing a graphene based layer on a substrate;
- b) providing said AlN nucleation /buffer layer having conformal coverage on entire graphene based layer; and
- c) providing thereon said AlN nucleation /buffer layer having conformal coverage, at least one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom graphene based group III nitride semiconducting films of desired thickness.

15. A method as claimed in anyone of claims 13 or 14 wherein said nitride nucleation /buffer layer is grown on said graphene layer such as to achieve said conformal coverage on entire graphene based layer followed by growing thereon said nitride nucleation /buffer layer the said nitride semiconducting film involving a semiconductor deposition system and following one or more of techniques selected from metal organic chemical vapor deposition (MOCVD), metal organic vapour phase epitaxy (MOVPE), solid or gas source molecular beam epitaxy (MBE), and hydride vapor phase epitaxy (HVPE).

16. A method as claimed in claim 13 wherein said nitride semiconducting film is grown in one or more orientations selected from polar, non-polar and semi-polar.

17. A method as claimed in claim 13 wherein said step (b) of providing a nucleation /buffer layer having conformal coverage on entire graphene based layer comprises the steps of

- (i) surface conditioning of the graphene based layer on the substrate followed by thermal cleaning in the temperature range of 900°C to 1100°C for 3 to 10min followed by cooling;
- (ii) growing stagewise said nitride nucleation /buffer layer involving required metalorganic and hydride precursors for nucleation of desired thickness under required system pressure and temperature.

18. A method as claimed in anyone of claims 14 to 17 wherein said step of providing AlN as nucleation /buffer layer comprises growing said nucleation /buffer layer involving precursors for nucleation involving low pressure in the range of 20 to 100 Torr following stepwise growth preferably involving either (A) two stage growth comprising (i) following a first stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 700 to 800 °C followed by (ii) second stage growth for thickness in the range of 25 to 40nm at temperature in the range of 1000 to 1100 °C or (B) three stage growth (i) following a first stage growth for thickness in the range of 10 to 20 nm at temperature in

the range of 600 to 700 °C (ii) second stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 850 to 950 °C and (iii) third stage growth for thickness in the range of 20 to 30 nm at temperature in the range of 1000 to 1100 °C .

5 19. A method as claimed in anyone of claims 13 to 18 wherein said step (c) of providing thereon said nitride nucleation /buffer layer, the group III nitride semiconducting film comprises the steps of providing required metalorganic and hydride precursors in the pressure ranging from 20 to 760 Torr, temperature ranging from 530 to 1100 °C, depending on the particular III-Nitride film deposited.

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20. A method as claimed in anyone of claims 13 to 19 for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material the said atleast one nucleation /buffer layer is grown in said semipolar orientation (10-11) involving precursors for nucleation and growth in the preferred temperature range of 600 to 1100  
15 °C and pressure in the range of 20 to 100 Torr and with selective V/III ratio in the range of 3500 to 10000.

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21. A method as claimed in claim 20 wherein for providing a preferred semipolar orientation (10-11) of Group III-nitride semiconducting material, said AlN as nucleation /buffer layer is grown in said semipolar orientation (10-11) involving precursors for nucleation and growth involving trimethylaluminium, ammonia and hydrogen carrier gas in the preferred temperature range of 600 to 1100°C preferably about 1000 °C and pressure in the range of 20 to 100 Torr, preferably 50 Torr and with selective V/III ratio in the range of 2500 to 10000 preferably above 3500.

25

22. A method as claimed in anyone of claims 13 to 21 wherein for providing preferred semipolar orientation (10-11) of GaN semiconducting film provided thereon said nitride nucleation /buffer layer comprises growing the GaN film involving trimethylgallium, ammonia and hydrogen carrier gas, at 50 to 200 Torr preferably 50 Torr reactor  
30 pressure at temperature 1000 to 1100°C preferably of 1040°C to thereby obtain semipolar oriented said GaN group III nitride semiconducting film as a single phase material.

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23. A method as claimed in anyone of claims 13 to 21 for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material wherein providing thereon said AlN nitride nucleation /buffer layer, preferably AlGaIn as the group III nitride semiconducting film comprises growing said Group III-nitride film involving selective precursor involving trimethylgallium, trimethylaluminium and ammonia and

hydrogen carrier gas, at 50 to 100 Torr preferably 50 Torr reactor pressure at temperature 1000 to 1100°C preferably of 1040°C to thereby obtain semi-polar oriented said group III nitride semiconducting film comprising AlGa<sub>N</sub> semi-polar (10-11) layer adapted as a single phase material.

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24. A method as claimed in anyone of claims 13 to 21 for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material wherein providing thereon said AlN nitride nucleation /buffer layer, InN or InGa<sub>N</sub> or as the group III nitride semiconducting film comprises growing the Group III-nitride film involving selective precursor involving trimethylindium, trimethylgallium, and ammonia and nitrogen carrier gas, at 200 to 500 Torr reactor pressure at temperature 530 to 800°C to thereby obtain semi-polar oriented said group III nitride semiconducting film comprising InN semi-polar (10-11) layer or InGa<sub>N</sub> semi-polar (10-11) layer adapted as a single phase material.

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25. A method as claimed in anyone of claims 13 to 24 wherein said substrate is selected from a group comprising of Sapphire, patterned Sapphire, Silicon, Silicon Oxide/Dioxide coated Silicon, Silicon Nitride coated Silicon, Silicon Carbide and Glass also comprising releasable sacrificial substrate layers including silicon oxide/dioxide, silicon nitride, spin-on-glass, polyimides.

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26. A method as claimed in claim 17 wherein said substrate is surface conditioned prior to deposition of said nitride semiconducting film preferably by exposure to oxygen plasma after which thermal cleaning of the substrate is preferably achieved by heating under hydrogen flow just prior to growth.

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27. A method as claimed in anyone of claims 13 to 26 comprising obtaining free standing graphene based group III nitride semiconducting films comprising

a) providing said graphene based layer on a sacrificial substrate;

b) providing said nitride nucleation /buffer layer having conformal coverage on entire graphene based layer;

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c) providing thereon said nucleation /buffer layer having conformal coverage, atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)<sub>N</sub> to obtain therefrom graphene based group III nitride semiconducting films of desired thickness; and

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d) removing the sacrificial layer to thereby obtain free standing Group III-nitride semiconducting material.

28. A method as claimed in claim 27 wherein said sacrificial substrate is selected from silicon oxide/ dioxide, silicon nitride, spin-on-glass, polyimides which is removed preferably by chemical etching of said sacrificial silicon dioxide layer below said graphene layer using HF/buffered HF.

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29. An optoelectronic device comprising Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N on said nitride nucleation /buffer layer with or without a suitable substrate.

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30. A semiconducting material adapted for facilitating epitaxial growth of semiconducting films as epilayer thereon comprising of graphene based layer and atleast one nitride nucleation /buffer layer comprising an alloy selected from combinations of alloy family (Al, In, Ga)N having conformal coverage of entire graphene surface with or without a suitable substrate.

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## AMENDED CLAIMS

received by the International Bureau on 19 August 2013 (19.08.13)

1. Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one aluminum nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface in semi-polar orientation and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N with semi-polar orientation on said aluminum nitride nucleation /buffer layer.
2. Group III-nitride semiconducting material as claimed in claim 1 wherein said group III-nitride semiconducting films of (Al, Ga, In, B) N with semi-polar orientation comprise at least one or more layers of dissimilar compositions within the alloy family of (Al,Ga,In,B)N
3. Group III-nitride semiconducting material as claimed in anyone of claims 1 or 2 wherein graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting film is planar with semi-polar orientation and selected from the group comprising of GaN, AlN, InN, AlGaN, AlInN, InGaN and AlGaInN.
4. Group III-nitride semiconducting material as claimed in anyone of the preceding claims wherein said graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting films comprise one or more layers of dissimilar compositions of the (Al, Ga, In, B) N alloy family selected from at least one or more of: GaN, AlN, InN alloys; ternary alloys of AlGaN, AlInN, InGaN; or quaternary alloys of AlGaInN and the like, in said film.
5. Group III-nitride semiconducting material as claimed in anyone of the preceding claims wherein said graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting films comprise free standing graphene-aluminum nitride nucleation /buffer layer based films with semi-polar orientation selected from (10-11), (11-22), (10-13) as a single phase material.
6. Group III-nitride semiconducting material as claimed in anyone of the preceding claims comprising said graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting free standing films with semi-polar orientation shaped and configured for variety of applications.

7. Group III-nitride semiconducting material as claimed in anyone of the preceding claims comprising said graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting films with semi-polar orientation on suitable substrates including rigid substrates preferably including glass, transparent conducting oxide (TCO) coated glass and/or flexible substrates preferably including plastics, metal foils.

8. Group III-nitride semiconducting material as claimed in any of the preceding claims comprising said graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting films with semi-polar orientation on suitable substrates including sapphire, patterned sapphire, silicon, silicon oxide /dioxide coated silicon, silicon nitride coated silicon, silicon carbide and glass.

9. Group III-nitride semiconducting material as claimed in any of the preceding claims comprising graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting films with semi-polar orientation adapted as free standing films on releasable sacrificial substrate layers including silicon oxide/dioxide, silicon nitride, spin-on-glass, polyimides.

10. Group III-nitride semiconducting material as claimed in any of the preceding claims comprising graphene-aluminum nitride nucleation /buffer layer based group III-nitride semiconducting films with semi-polar orientation scalable to a large area including from 10s to about 100s of cm<sup>2</sup> adapted for various optoelectronic devices.

11. A method of manufacture of Group III-nitride semiconducting material with semi-polar orientation as claimed in anyone of claims 1 to 10 comprising

- a) providing a graphene based layer on a substrate;
- b) providing said aluminum nitride nucleation /buffer layer with semi-polar orientation such as to obtain conformal coverage on entire graphene based layer comprising growing said AlN nucleation /buffer layer in said semipolar orientation on graphene involving precursors for nucleation and growth in the temperature range 600°C to 1100 °C and pressure of 20 to 100 Torr and with selective V/III ratio in the range of at least 3500 to 10000; and
- c) providing thereon said nucleation/buffer layer, having thus obtained semi-polar orientation with conformal coverage on the entire graphene surface, atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom

graphene-aluminum nitride nucleation /buffer layer based group III nitride semiconducting films with semi-polar orientation of desired thickness.

12. A method as claimed in claim 11 wherein said nitride nucleation /buffer layer is grown on said graphene layer involving a semiconductor deposition system and following one or more of techniques selected from metal organic chemical vapor deposition (MOCVD), metal organic vapour phase epitaxy (MOVPE),, and hydride vapor phase epitaxy (HVPE).

13. A method as claimed in claim 11 wherein said step (b) of providing a AlN nucleation /buffer layer with semi-polar orientation having conformal coverage on entire graphene based layer comprises the steps of

- (i) surface conditioning of the graphene based layer on the substrate followed by thermal cleaning in the temperature range of 900°C to 1100°C for 3 to 10 min followed by cooling;
- (ii) growing stagewise said aluminum nitride nucleation /buffer layer involving required metalorganic and hydride precursors for nucleation with semi-polar orientation of desired thickness under required system pressure and temperature and selective V/III ratio.

14. A method as claimed in anyone of claims 11 to 13 wherein said step of providing AlN as nucleation /buffer layer with semi-polar orientation comprises growing said nucleation /buffer layer involving precursors for nucleation involving low pressure in the range of 20 to 100 Torr following stepwise growth preferably involving either (A) two stage growth comprising (i) following a first stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 700 to 800 °C followed by (ii) second stage growth for thickness in the range of 25 to 40 nm at temperature in the range of 1000 to 1100 °C or (B) three stage growth (i) following a first stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 600 to 700 °C (ii) second stage growth for thickness in the range of 10 to 20 nm at temperature in the range of 850 to 950 °C and (iii) third stage growth for thickness in the range of 20 to 30 nm at temperature in the range of 1000 to 1100 °C .

15. A method as claimed in anyone of claims 11 to 14 wherein said step (c) of providing thereon said AlN nitride nucleation /buffer layer, the group III nitride semiconducting film comprises the steps of providing required metalorganic and hydride precursors in the

pressure ranging from 20 to 760 Torr, temperature ranging from 530 to 1100 °C, depending on the particular III-Nitride film deposited.

16. A method as claimed in claims 11 to 14 wherein for providing a preferred semipolar orientation (10-11) of Group III-nitride semiconducting material, said AlN as nucleation /buffer layer is grown in said semipolar orientation (10-11) involving precursors for nucleation and growth involving trimethylaluminium, ammonia and hydrogen carrier gas at a temperature of about 1000 °C and pressure about 50 Torr and with selective V/III ratio above 3500.

17. A method as claimed in anyone of claims 11 to 16 wherein for providing preferred semi-polar orientation (10-11) of GaN semiconducting film provided thereon said aluminum nitride nucleation /buffer layer comprises growing the GaN film involving trimethylgallium, ammonia and hydrogen carrier gas, at about 50 Torr reactor pressure at temperature of about 1040°C to thereby obtain semi-polar oriented said GaN group III nitride semiconducting film as a single phase material.

18. A method as claimed in anyone of claims 11 to 17 for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material wherein providing thereon said AlN nitride nucleation /buffer layer, preferably AlGaN as the group III nitride semiconducting film comprises growing said Group III-nitride film involving selective precursor involving trimethylgallium, trimethylaluminium and ammonia and hydrogen carrier gas, at about 50 Torr reactor pressure at temperature of about 1040°C to thereby obtain semi-polar oriented said group III nitride semiconducting film comprising AlGaN semi-polar (10-11) layer adapted as a single phase material.

19. A method as claimed in anyone of claims 11 to 18 for providing preferred semipolar orientation (10-11) of Group III-nitride semiconducting material wherein providing thereon said AlN nitride nucleation /buffer layer, InN or InGaN or as the group III nitride semiconducting film comprises growing the Group III-nitride film involving selective precursor involving trimethylindium, trimethylgallium, and ammonia and nitrogen carrier gas, at 200 to 500 Torr reactor pressure at temperature 530 to 800°C to thereby obtain semi-polar oriented said group III nitride semiconducting film comprising InN semi-polar (10-11) layer or InGaN semi-polar (10-11) layer adapted as a single phase material.

20. A method as claimed in anyone of claims 11 to 19 wherein said substrate is selected from a group comprising of Sapphire, patterned Sapphire, Silicon, Silicon Oxide/Dioxide coated Silicon, Silicon Nitride coated Silicon, Silicon Carbide and Glass also comprising releasable sacrificial substrate layers including silicon oxide/dioxide, silicon nitride, spin-on-glass, polyimides.

21. A method as claimed in claim 13 wherein said substrate is surface conditioned prior to deposition of said nitride semiconducting film preferably by exposure to oxygen plasma after which thermal cleaning of the substrate is preferably achieved by heating under hydrogen flow just prior to growth.

22. A method as claimed in anyone of claims 11 to 21 comprising obtaining free standing graphene based group III nitride semiconducting films with semi-polar orientation comprising

- a) providing said graphene based layer on a sacrificial substrate;
- b) providing said aluminum nitride nucleation /buffer layer with semi-polar orientation such as to obtain conformal coverage on entire graphene based layer comprising growing said AlN nucleation /buffer layer in said semipolar orientation on graphene involving precursors for nucleation and growth in the temperature range 600°C to 1100 °C and pressure of 20 to 100 Torr and with selective V/III ratio in the range of at least 3500 to 10000;
- c) providing thereon said nucleation /buffer layer having thus obtained semi-polar orientation with conformal coverage on the entire graphene surface, atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N to obtain therefrom graphene-aluminum nitride nucleation /buffer layer based group III nitride semiconducting films with semi-polar orientation of desired thickness; and
- d) removing the sacrificial layer to thereby obtain free standing Group III-nitride semiconducting material with semi-polar orientation.

23. A method as claimed in claim 22 wherein said sacrificial substrate is selected from silicon oxide/ dioxide, silicon nitride, spin-on-glass, polyimides which is removed preferably by chemical etching of said sacrificial silicon dioxide layer below said graphene layer using HF/buffered HF.

24. An optoelectronic device comprising Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one AlN nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface in semi-polar orientation and atleast one group III-nitride semiconducting film selected from alloy family of (Al,Ga,In,B)N with semi-polar orientation on said aluminum nitride nucleation /buffer layer with or without a suitable substrate.

25. A semiconducting material adapted for facilitating epitaxial growth of semiconducting films as epilayer thereon in semi-polar orientation comprising of graphene based layer and atleast one AlN nitride nucleation /buffer layer having conformal coverage of entire graphene surface in semi-polar orientation with or without a suitable substrate.

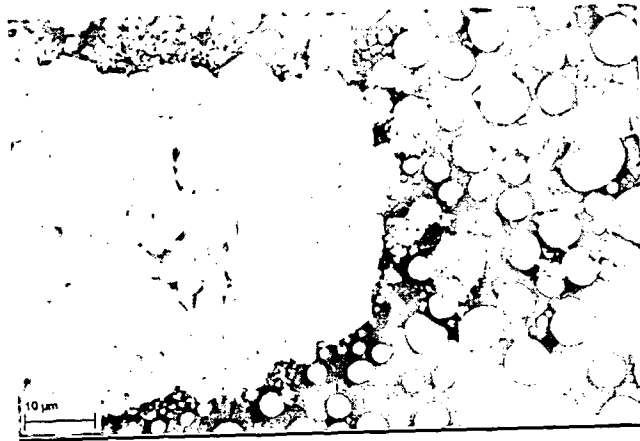
**STATEMENT UNDER ARTICLE 19 OF PCT**

Amended claims are directed to further clarify and qualify the advancement residing in Group III-nitride semiconducting material comprising of graphene based layer having thereon atleast one aluminum nitride nucleation /buffer layer adapted for conformal coverage of entire graphene surface in semi-polar orientation and atleast one group III-nitride semiconducting film selected from alloy family of (Al, Ga, In, B)N with semi-polar orientation on said aluminum nitride nucleation /buffer layer, and a process for manufacturing the same in said semi-polar orientation involving selective process parameters of pressure, temperature and V/III ratio in CVD (chemical vapour deposition) growth conditions. Basically the amendments qualify the claims further in keeping with the inventive steps that enable the attainment of the specific semi-polar orientation of the semiconducting film selected from alloy family of (Al,Ga,In,B)N only because of the attained graphene based aluminum nitride nucleation /buffer layer in semi-polar orientation adapted for conformal coverage of entire graphene surface.

The amendments in the claims are directed to qualify the claimed invention and do not extend beyond the disclosure and directions in the international application as filed.

**Fig. 1**

**Fig. 2(a)**



**Fig. 2(b)**

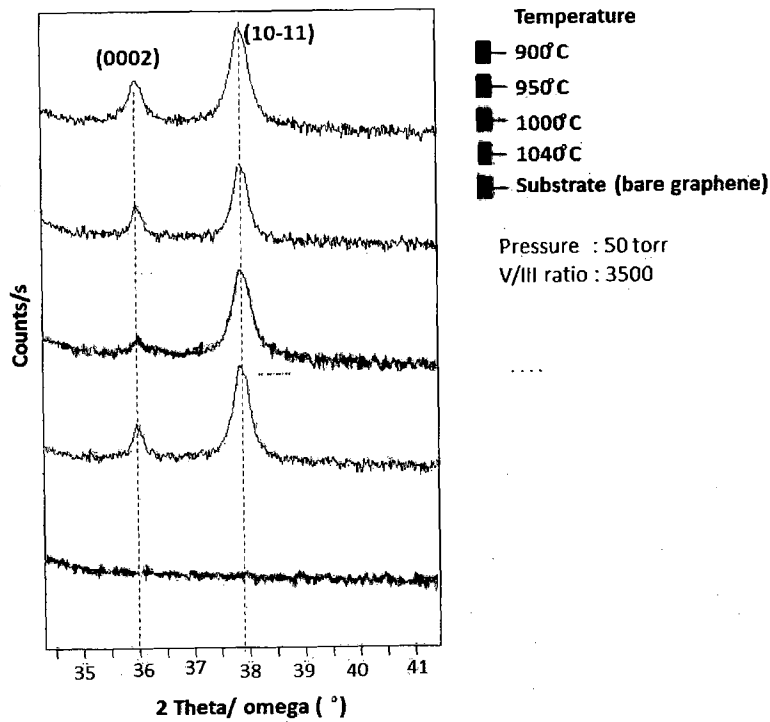


Fig. 3(a)

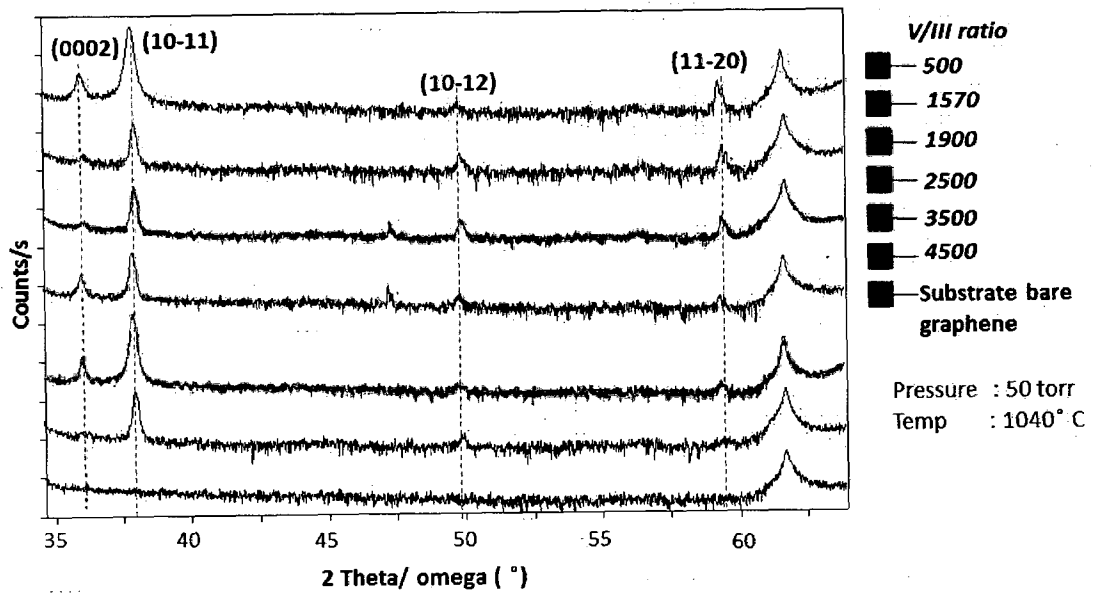


Fig. 3(b)

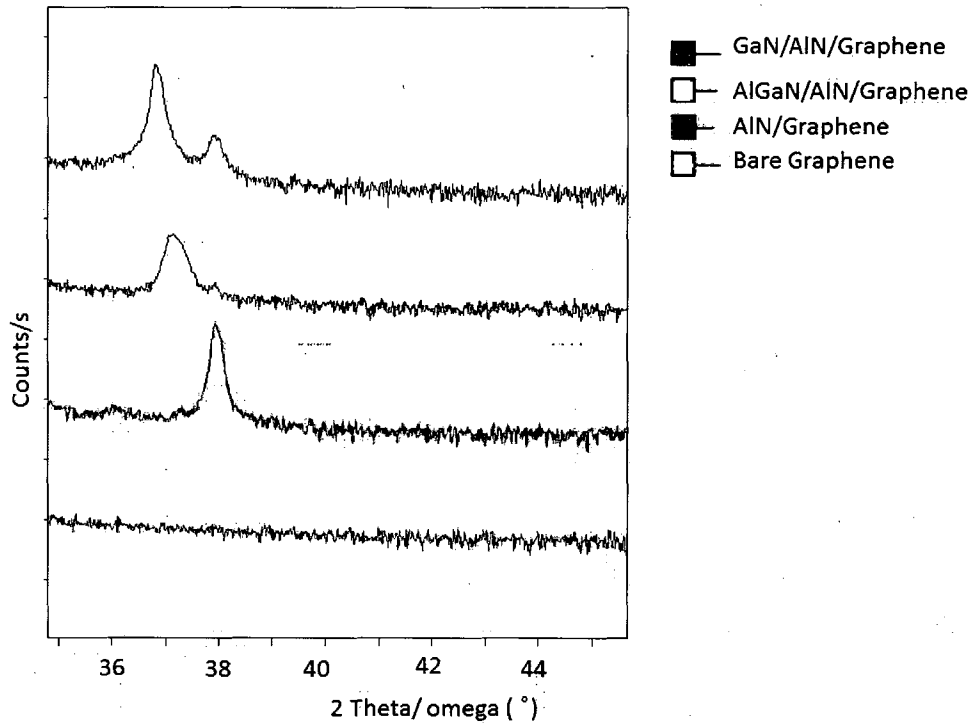


Fig. 4

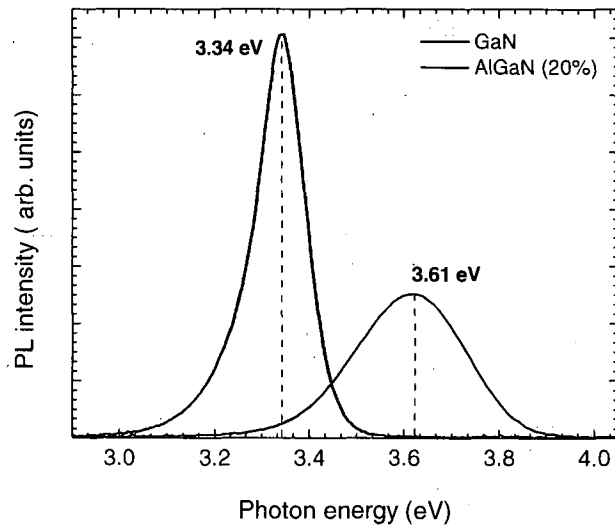


Fig. 5

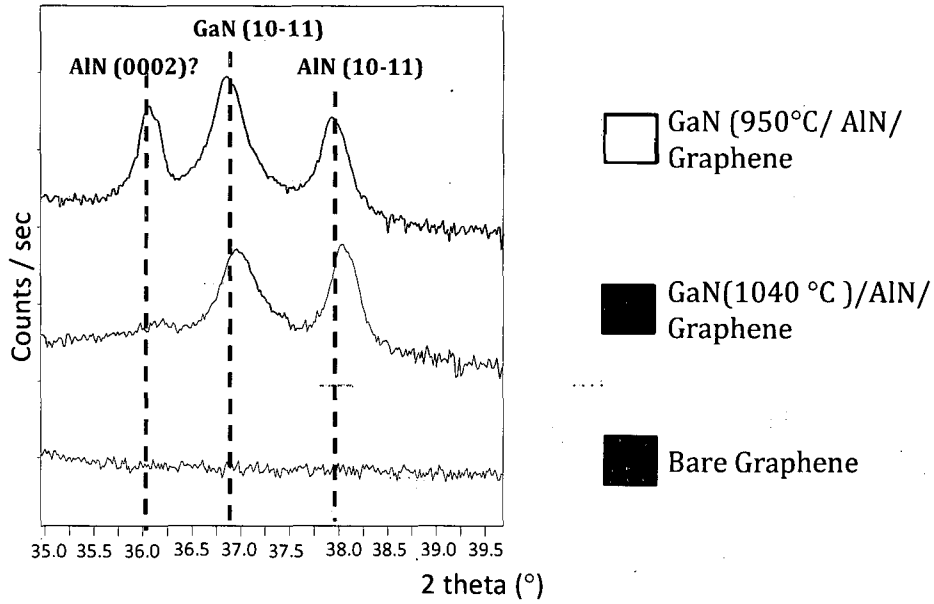


Fig. 6

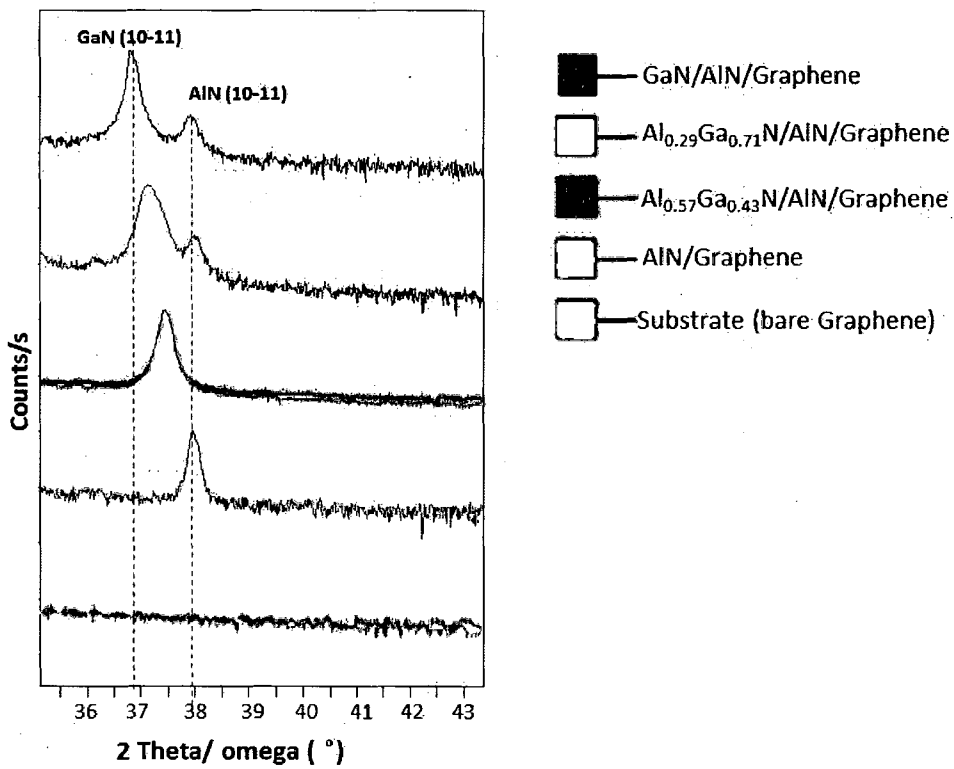


Fig. 7

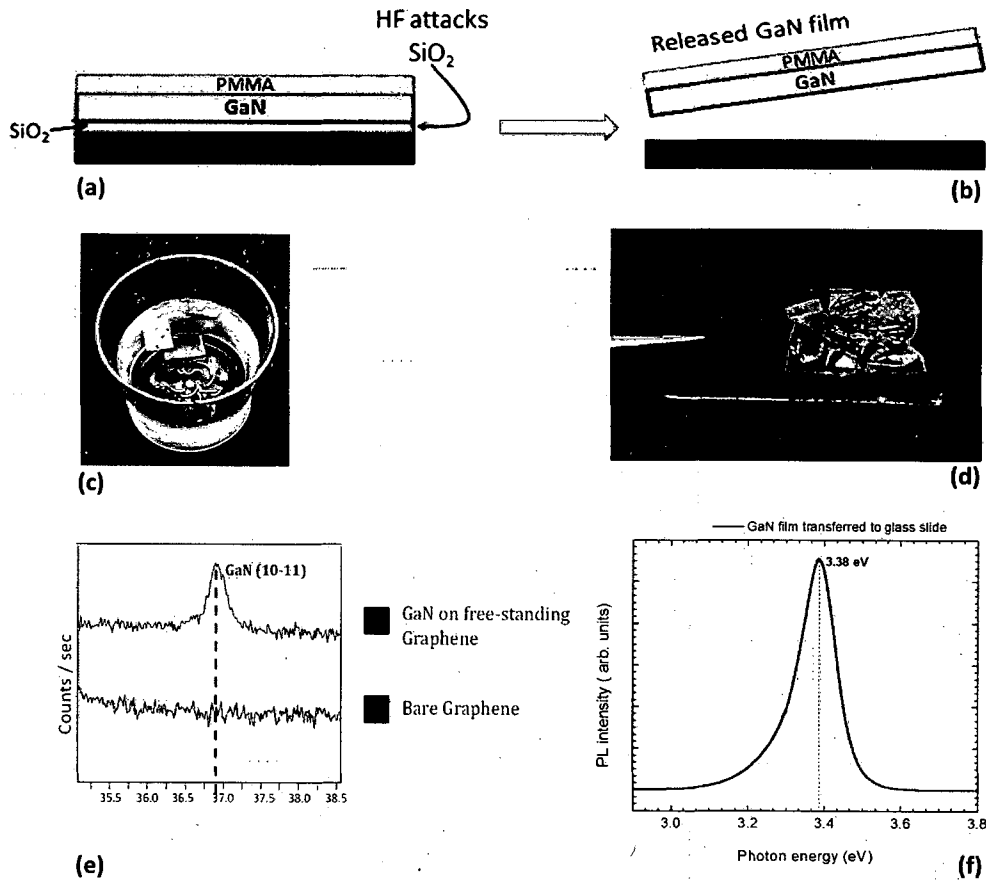


Fig. 8a-f

# INTERNATIONAL SEARCH REPORT

International application No <b>PCT/IN2012/000287</b>
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. H01L21/02 H01L21/20 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) H01L C30B				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, INSPEC, COMPENDEX				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2010/320445 A1 (OGIHARA MITSUHIKO [JP] ET AL) 23 December 2010 (2010-12-23) paragraphs [0015] - [0023], [0054] - [0095], [0114] - [0134]; claims 12,15; figures 1-23 -----	1-25, 27-30		
X	US 2012/056237 A1 (CHOI JUN-HEE [KR] ET AL) 8 March 2012 (2012-03-08)  paragraphs [0030] - [0039], [0051] - [0056], [0063] - [0073]; figures 1-3,7,9 ----- -/--	1-5,7-9, 11,13, 15-26, 28-30		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</td> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> See patent family annex.</td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
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21 November 2012	13/12/2012			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Norga, Gerd			

INTERNATIONAL SEARCH REPORT

International application No  
PCT/IN2012/000287

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>JP 2011 009268 A (OKI DATA KK; OKI DIGITAL IMAGING CORP) 13 January 2011 (2011-01-13)</p> <p>* the Abstract; figures 1 - 19 *</p>	<p>1-6,8, 10,11, 13-15, 17-24, 26,27, 29,30</p>
X	<p>KR 2012 0029248 A (SAMSUNG LED CO LTD [KR]) 26 March 2012 (2012-03-26)</p> <p>paragraph [0005] - paragraph [0040]; figures 1, 2a, 2b, 3, 4</p>	<p>1-6,8, 10,11, 13, 15-24, 26,27, 29,30</p>
A	<p>WON IL PARK ET AL: "Inorganic nanostructures grown on graphene layers", NANOSCALE, vol. 3, no. 9, 2011, pages 3522-3533, XP002687653, ROYAL SOCIETY OF CHEMISTRY UK ISSN: 2040-3364 the whole document</p>	<p>1-30</p>
A	<p>YOO H ET AL: "Microstructures of GaN thin films grown on graphene layers", ADVANCED MATERIALS 20120124 WILEY-VCH VERLAG DEU, vol. 24, no. 4, 24 January 2012 (2012-01-24), pages 515-518, XP002687655, DOI: 10.1002/ADMA.201103829 * " Experimental Section" *</p>	<p>1-30</p>

# INTERNATIONAL SEARCH REPORT

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International application No  
PCT/IN2012/000287

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		EP 2267796 A2	29-12-2010
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JP 2011009268	A	NONE	
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