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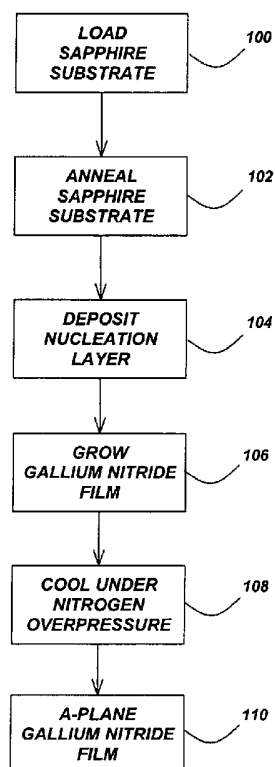
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(54) Title: NON-POLAR A-PLANE GALLIUM NITRIDE THIN FILMS GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION

(57) Abstract: Non-polar (1120) a-plane gallium nitride (GaN) films with planar surfaces are grown on (1102) r-plane sapphire substrates by employing a low temperature nucleation layer as a buffer layer prior to a high temperature growth of the non-polar (1120) a-plane GaN thin films.



WO 03/089695 A1



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NON-POLAR A-PLANE GALLIUM NITRIDE THIN FILMS GROWN BY
METALORGANIC CHEMICAL VAPOR DEPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. § 119(e) of the following co-pending and commonly-assigned United States Provisional Patent Application Serial No. 60/372,909, entitled "NON-POLAR GALLIUM NITRIDE BASED THIN
5 FILMS AND HETEROSTRUCTURE MATERIALS," filed on April 15, 2002, by Michael D. Craven, Stacia Keller, Steven P. DenBaars, Tal Margalith, James S. Speck, Shuji Nakamura, and Umesh K. Mishra, attorneys docket number 30794.95-US-P1, which application is incorporated by reference herein.

This application is related to the following co-pending and commonly-
10 assigned United States Utility Patent Applications:

Serial No. --/---,---, entitled "NON-POLAR (AL,B,IN,GA)N QUANTUM
WELL AND HETEROSTRUCTURE MATERIALS AND DEVICES," filed on same
date herewith, by Michael D. Craven, Stacia Keller, Steven P. DenBaars, Tal
Margalith, James S. Speck, Shuji Nakamura, and Umesh K. Mishra, attorneys docket
15 number 30794.101-US-U1; and

Serial No. --/---,---, entitled "DISLOCATION REDUCTION IN NON-
POLAR GALLIUM NITRIDE THIN FILMS," filed on same date herewith, by
Michael D. Craven, Steven P. DenBaars and James S. Speck, attorneys docket
number 30794.102-US-U1;

20 both of which applications are incorporated by reference herein.

1. Field of the Invention.

The invention is related to semiconductor materials, methods, and devices, and
more particularly, to non-polar a-plane gallium nitride (GaN) thin films grown by
25 metalorganic chemical vapor deposition (MOCVD).

2. Description of the Related Art.

(Note: This application references a number of different patents, applications and/or publications as indicated throughout the specification by one or more reference numbers. A list of these different publications ordered according to these reference
5 numbers can be found below in the section entitled "References." Each of these publications is incorporated by reference herein.)

Polarization in wurtzite III-nitride compounds has attracted increased attention due to the large effect polarization-induced electric fields have on heterostructures commonly employed in nitride-based optoelectronic and electronic devices. Nitride-
10 based optoelectronic and electronic devices are subject to polarization-induced effects because they employ nitride films grown in the polar c-direction [0001], the axis along which the spontaneous and piezoelectric polarization of nitride films are aligned. Since the total polarization of a nitride film depends on the composition and strain state, discontinuities exist at interfaces between adjacent device layers and are
15 associated with fixed sheet charges that give rise to internal electric fields.

Polarization-induced electric fields, although advantageous for two-dimensional electron gas (2DEG) formation in nitride-based transistor structures, spatially separate electrons and hole wave functions in quantum well (QW) structures, thereby reducing carrier recombination efficiencies in QW based devices, such as
20 laser diodes and light emitting diodes. See References 1. A corresponding reduction in oscillator strength and red-shift of optical transitions have been reported for AlGaIn/GaN and GaN/InGaIn quantum wells grown along the GaN c-axis. See References 2–7.

A potential means of eliminating the effects of these polarization-induced
25 fields is through the growth of structures in directions perpendicular to the GaN c-axis (non-polar) direction. For example, m-plane AlGaIn/GaN quantum wells have recently been grown on lithium aluminate substrates via plasma-assisted molecular beam epitaxy (MBE) without the presence of polarization-induced electric fields along the growth direction. See Reference 8.

Growth of a-plane nitride semiconductors also provides a means of eliminating polarization-induced electric field effects in wurtzite nitride quantum structures. For example, in the prior art, a-plane GaN growth had been achieved on r-plane sapphire via MOCVD and molecular beam epitaxy (MBE). See References 9-15. However, the film growth reported by these early efforts did not utilize a low temperature buffer layer and did not possess smooth planar surfaces, and therefore, these layers were poorly suited for heterostructure growth and analysis. Consequently, there is a need for improved methods of growing films that exhibit improved surface and structural quality as compared to previously reported growth of GaN on r-plane sapphire via MOCVD.

SUMMARY OF THE INVENTION

The present invention describes a method for growing device-quality non-polar a-plane GaN thin films via MOCVD on r-plane sapphire substrates. The present invention provides a pathway to nitride-based devices free from polarization-induced effects, since the growth direction of non-polar a-plane GaN thin films is perpendicular to the polar c-axis. Polarization-induced electric fields will have minimal effects, if any, on (Al,B,In,Ga)N device layers grown on non-polar a-plane GaN thin films.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

FIG. 1 is a flowchart that illustrates the steps of the MOCVD process for the growth of non-polar $(11\bar{2}0)$ a-plane GaN thin films on $(1\bar{1}20)$ r-plane sapphire, according to the preferred embodiment of the present invention;

FIG. 2(a) shows a 2θ - ω diffraction scan that identifies the growth direction of the GaN film as $(11\bar{2}0)$ a-plane GaN;

FIG. 2(b) is a compilation of off-axis ϕ scans used to determine the in-plane epitaxial relationship between GaN and r-sapphire, wherein the angle of inclination ψ used to access the off-axis reflections is noted for each scan;

FIG. 2(c) is a schematic illustration of the epitaxial relationship between the
5 GaN and r-plane sapphire;

FIGS. 3(a) and 3(b) are cross-sectional and plan-view transmission electron microscopy (TEM) images, respectively, of the defect structure of the a-plane GaN films on r-plane sapphire; and

FIGS. 4(a) and 4(b) are atomic force microscopy (AFM) amplitude and height
10 images, respectively, of the surface of the as-grown a-plane GaN films.

DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to
15 the accompanying drawings which form a part hereof, and in which is shown by way of illustration a specific embodiment in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present invention.

20 Overview

The present invention describes a method for growing device quality non-polar $(11\bar{2}0)$ a-plane GaN thin films via MOCVD on $(1\bar{1}02)$ r-plane sapphire substrates. The method employs a low-temperature buffer layer grown at atmospheric pressure to initiate the GaN growth on r-plane sapphire. Thereafter, a high
25 temperature growth step is performed at low pressures, e.g., ~ 0.1 atmospheres (atm) in order to produce a planar film.

Planar growth surfaces have been achieved using the present invention. Specifically, the in-plane orientation of the GaN with respect to the r-plane sapphire

substrate has been confirmed to be $[0001]_{\text{GaN}} \parallel [\bar{1}101]_{\text{sapphire}}$ and $[\bar{1}100]_{\text{GaN}} \parallel [11\bar{2}0]_{\text{sapphire}}$.

The resulting films possess surfaces that are suitable for subsequent growth of (Al,B,In,Ga)N device layers. Specifically, polarization-induced electric fields will have minimal effects, if any, on (Al,B,In,Ga)N device layers grown on non-polar a-plane GaN base layers.

Process Steps

FIG. 1 is a flowchart that illustrates the steps of the MOCVD process for the growth of non-polar $(11\bar{2}0)$ a-plane GaN thin films on a $(1\bar{1}20)$ r-plane sapphire substrate, according to the preferred embodiment of the present invention. The growth process was modeled after the two-step process that has become the standard for the growth of c-GaN on c-sapphire. See Reference 16.

Block 100 represents loading of a sapphire substrate into a vertical, close-spaced, rotating disk, MOCVD reactor. For this step, epi-ready sapphire substrates with surfaces crystallographically oriented within $\pm 2^\circ$ of the sapphire r-plane $(1\bar{1}20)$ may be obtained from commercial vendors. No ex-situ preparations need be performed prior to loading the sapphire substrate into the MOCVD reactor, although ex-situ cleaning of the sapphire substrate could be used as a precautionary measure.

Block 102 represents annealing the sapphire substrate in-situ at a high temperature ($>1000^\circ\text{C}$), which improves the quality of the substrate surface on the atomic scale. After annealing, the substrate temperature is reduced for the subsequent low temperature nucleation layer deposition.

Block 104 represents depositing a thin, low temperature, low pressure, nitride-based nucleation layer as a buffer layer on the sapphire substrate. In the preferred embodiment, the nucleation layer is comprised of, but is not limited to, 1-100 nanometers (nm) of GaN and is deposited at low temperature, low pressure depositing conditions of approximately $400\text{-}900^\circ\text{C}$ and 1 atm. Such layers are commonly used in

the heteroepitaxial growth of c-plane (0001) nitride semiconductors. Specifically, this depositing step initiates GaN growth on the r-plane sapphire substrate.

After depositing the nucleation layer, the reactor temperature is raised to a high temperature, and Block 106 represents growing the non-polar (11 $\bar{2}$ 0) a-plane GaN thin films on the substrate. In the preferred embodiment, the high temperature growth conditions comprise, but are not limited to, approximately 1100°C growth temperature, approximately 0.2 atm or less growth pressure, 30 μ mol per minute Ga flow, and 40,000 μ mol per minute N flow, thereby providing a V/III ratio of approximately 1300). In the preferred embodiment, the precursors used as the group III and group V sources are trimethylgallium and ammonia, respectively, although alternative precursors could be used as well. In addition, growth conditions may be varied to produce different growth rates, e.g., between 5 and 9 Å per second, without departing from the scope of the present invention. Non-polar GaN approximately 1.5 μ m thick have been grown and characterized.

Upon completion of the high temperature growth step, Block 108 represents cooling the non-polar (11 $\bar{2}$ 0) a-plane GaN thin films under a nitrogen overpressure.

Finally, Block 110 represents the end result of the processing steps, which is a non-polar (11 $\bar{2}$ 0) a-plane GaN film on an r-plane sapphire substrate. Potential device layers to be manufactured using these process steps to form a non-polar (11 $\bar{2}$ 0) a-plane GaN base layer for subsequent device growth include laser diodes (LDs), light emitting diodes (LEDs), resonant cavity LEDs (RC-LEDs), vertical cavity surface emitting lasers (VCSELs), high electron mobility transistors (HEMTs), heterojunction bipolar transistors (HBTs), heterojunction field effect transistors (HFETs), and UV and near-UV photodetectors.

25

Experimental Results

The crystallographic orientation and structural quality of the as-grown GaN films and r-plane sapphire were determined using a Philips™ four-circle, high-resolution, x-ray diffractometer (HR-XRD) operating in receiving slit mode with four

bounce Ge(220)-monochromated Cu K α radiation and a 1.2 mm slit on the detector arm. Convergent beam electron diffraction (CBED) was used to determine the polarity of the a-GaN films with respect to the sapphire substrate. Plan-view and cross-section transmission electron microscopy (TEM) samples, prepared by wedge
 5 polishing and ion milling, were analyzed to define the defect structure of a-GaN. A Digital Instruments D3000 Atomic Force Microscope (AFM) in tapping mode produced images of the surface morphology.

FIG. 2(a) shows a 2θ - ω diffraction scan that identifies the growth direction of the GaN film as (11 $\bar{2}$ 0) a-plane GaN. The scan detected sapphire (1 $\bar{1}$ 02), (2 $\bar{2}$ 04), and
 10 GaN (11 $\bar{2}$ 0) reflections. Within the sensitivity of these measurements, no GaN (0002) reflections corresponding to $2\theta = 34.604^\circ$ were detected, indicating that there is no c-plane (0002) content present in these films, and thus instabilities in the GaN growth orientation are not a concern.

FIG. 2(b) is a compilation of off-axis ϕ scans used to determine the in-plane
 15 epitaxial relationship between GaN and r-sapphire, wherein the angle of inclination ψ used to access the off-axis reflections is noted for each scan. Having confirmed the a-plane growth surface, off-axis diffraction peaks were used to determine the in-epitaxial relationship between the GaN and the r-sapphire. Two sample rotations ϕ and ψ were adjusted in order to bring off-axis reflections into the scattering plane of
 20 the diffractometer, wherein ϕ is the angle of rotation about the sample surface normal and ψ is the angle of sample tilt about the axis formed by the intersection of the Bragg and scattering planes. After tilting the sample to the correct ψ for a particular off-axis reflection, ϕ scans detected GaN (10 $\bar{1}$ 0), (10 $\bar{1}$ 1), and sapphire (0006) peaks, as shown in FIG. 2(b). The correlation between the ϕ positions of these peaks determined the
 25 following epitaxial relationship: $[0001]_{\text{GaN}} \parallel [\bar{1}101]_{\text{sapphire}}$ and $[\bar{1}100]_{\text{GaN}} \parallel [11\bar{2}0]_{\text{sapphire}}$.

FIG. 2(c) is a schematic illustration of the epitaxial relationship between the GaN and r-plane sapphire. To complement the x-ray analysis of the crystallographic

orientation, the a-GaN polarity was determined using CBED. The polarity's sign is defined by the direction of the polar Ga-N bonds aligned along the GaN c-axis; the positive c-axis [0001] points from a gallium atom to a nitrogen atom. Consequently, a gallium-face c-GaN film has a [0001] growth direction, while a nitrogen-face c-GaN crystal has a $[000\bar{1}]$ growth direction. For a-GaN grown on r-sapphire, $[0001]_{\text{GaN}}$ is aligned with the sapphire c-axis projection $[\bar{1}101]_{\text{sapphire}}$, and therefore, the epitaxial relationships defined above are accurate in terms of polarity. Consequently, the positive GaN c-axis points in same direction as the sapphire c-axis projection on the growth surface (as determined via CBED). This relationship concurs with the epitaxial relationships previously reported by groups using a variety of growth techniques. See References 9, 12 and 14. Therefore, the epitaxial relationship is specifically defined for the growth of GaN on an r-plane sapphire substrate.

FIGS. 3(a) and 3(b) are cross-sectional and plan-view TEM images, respectively, of the defect structure of the a-plane GaN films on an r-plane sapphire substrate. These images reveal the presence of line and planar defects, respectively. The diffraction conditions for FIGS. 3(a) and 3(b) are $g = 0002$ and $g = 10\bar{1}0$, respectively.

The cross-sectional TEM image in FIG. 3(a) reveals a large density of threading dislocations (TD's) originating at the sapphire/GaN interface with line directions parallel to the growth direction $[11\bar{2}0]$. The TD density, determined by plan view TEM, was $2.6 \times 10^{10} \text{ cm}^{-2}$. With the TD line direction parallel to the growth direction, pure screw dislocations will have Burgers vectors aligned along the growth direction $b = \pm [11\bar{2}0]$ while pure edge dislocations will have $b = \pm [0001]$. The reduced symmetry of the a-GaN surface with respect to c-GaN complicates the characterization of mixed dislocations since the crystallographically equivalent $[11\bar{2}0]$ directions cannot be treated as the family $\langle 11\bar{2}0 \rangle$. Specifically, the possible Burgers vectors of mixed dislocations can be divided into three subdivisions: (1) $b = \pm$

$[\bar{1}\bar{2}10]b =$ and (3) $b = \pm [\bar{2}110]$, (2) $b = \pm [11\bar{2}0] \pm [0001]$, and (3) $b = \pm [11\bar{2}0] \pm [1\bar{2}10]$ and $b = \pm [11\bar{2}0] \pm [\bar{2}110]$.

In addition to line defects, the plan view TEM image in FIG. 3(b) reveals the planar defects observed in the a-GaN films. Stacking faults aligned perpendicular to the c-axis with a density of $3.8 \times 10^5 \text{ cm}^{-1}$ were observed in the plan-view TEM images. The stacking faults, commonly associated with epitaxial growth of close-packed planes, most likely originate on the c-plane sidewalls of three-dimensional (3D) islands that form during the initial stages of the high temperature growth. Consequently, the stacking faults are currently assumed to be intrinsic and terminated by Shockley partial dislocations of opposite sign. Stacking faults with similar characteristics were observed in a-plane AlN films grown on r-plane sapphire substrates. See Reference 17. The stacking faults have a common faulting plane parallel to the close-packed (0001) and a density of $\sim 3.8 \times 10^5 \text{ cm}^{-1}$.

Omega rocking curves were measured for both the GaN on-axis ($11\bar{2}0$) and off-axis ($10\bar{1}1$) reflections to characterize the a-plane GaN crystal quality. The full-width half-maximum (FWHM) of the on-axis peak was 0.29° ($1037''$), while the off-axis peak exhibited a larger orientational spread with a FWHM of 0.46° ($1659''$). The large FWHM values are expected since the microstructure contains a substantial dislocation density. According to the analysis presented by Heying et al. for c-GaN films on c-sapphire, on-axis peak widths are broadened by screw and mixed dislocations, while off-axis widths are broadened by edge-component TD's (assuming the TD line is parallel to the film normal). See Reference 18. A relatively large edge dislocation density is expected for a-GaN on r-sapphire due to the broadening of the off-axis peak compared to the on-axis peak. Additional microstructural analyses are required to correlate a-GaN TD geometry to rocking curve measurements.

FIGS. 4(a) and 4(b) are AFM amplitude and height images, respectively, of the surface of the as-grown a-plane GaN film. The surface pits in the AFM amplitude

image of FIG. 4(a) are uniformly aligned parallel to the GaN c-axis, while the terraces visible in the AFM height image of FIG. 4(b) are aligned perpendicular to the c-axis.

Although optically specular with a surface RMS roughness of 2.6 nm, the a-GaN growth surface is pitted on a sub-micron scale, as can be clearly observed in the AFM amplitude image shown in FIG. 4(a). It has been proposed that the surface pits are decorating dislocation terminations with the surface; the dislocation density determined by plan view TEM correlates with the surface pit density within an order of magnitude.

In addition to small surface pits aligned along GaN c-axis [0001], the AFM height image in FIG. 4(b) reveals faint terraces perpendicular to the c-axis. Although the seams are not clearly defined atomic steps, these crystallographic features could be the early signs of the surface growth mode. At this early point in the development of the a-plane growth process, neither the pits nor the terraces have been correlated to particular defect structures.

References

The following references are incorporated by reference herein:

1. I. P. Smorchkova, C. R. Elsass, J. P. Ibbetson, R. Vetury, B. Heying, P. Fini, E. Haus, S. P. DenBaars, J. S. Speck, and U. K. Mishra, J. Appl. Phys. 86, 4520 (1999).
2. O. Ambacher, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, W. J. Schaff, L. F. Eastman, R. Dimitrov, L. Wittmer, M. Stutzmann, W. Rieger, and J. Hilsenbeck, J. Appl. Phys. 85, 3222 (1999).
3. I. Jin Seo, H. Kollmer, J. Off, A. Sohmer, F. Scholz, and A. Hangleiter, Phys. Rev. B 57, R9435 (1998).
4. R. Langer, J. Simon, V. Ortiz, N. T. Pelekanos, A. Barski, R. Andre, and M. Godlewski, Appl. Phys. Lett. 74, 3827 (1999).
5. P. Lefebvre, J. Allegre, B. Gil, H. Mathieu, N. Grandjean, M. Leroux, J. Massies, and P. Bigenwald, Phys. Rev. B 59, 15363 (1999).

6. P. Lefebvre, A. Morel, M. Gallart, T. Taliercio, J. Allegre, B. Gil, H. Mathieu, B. Damilano, N. Grandjean, and J. Massies, *Appl. Phys. Lett.* 78, 1252 (2001).
7. T. Takeuchi, C. Wetzel, S. Yamaguchi, H. Sakai, H. Amano, I. Akasaki, Y. Kaneko, S. Nakagawa, Y. Yamaoka, and N. Yamada, *Appl. Phys. Lett.* 73, 1691 (1998).
8. P. Waltereit, O. Brandt, A. Trampert, H. T. Grahn, J. Menniger, M. Ramsteiner, M. Reiche, and K. H. Ploog, *Nature (London)* 406, 865 (2000).
9. T. Sasaki and S. Zembutsu, *J. Appl. Phys.* 61, 2533 (1987).
10. C. J. Sun and M. Razeghi, *Appl. Phys. Lett.* 63, 973 (1993).
11. T. Metzger, H. Angerer, O. Ambacher, M. Stutzmann, and E. Born, *Phys. Status Solidi B* 193, 391 (1996).
12. T. Lei, K. F. Ludwig, Jr., and T. D. Moustakas, *J. Appl. Phys.* 74, 4430 (1993).
13. C. R. Eddy, Jr., T. D. Moustakas, and J. Scanlon, *J. Appl. Phys.* 73, 448 (1993).
14. T. D. Moustakas, T. Lei, and R. J. Molnar, *Physica B* 185, 36 (1993).
15. K. Iwata, H. Asahi, K. Asami, R. Kuroiwa, and S. Gonda, *Jpn. J. Appl. Phys., Part 2* 36, L661 (1997).
16. H. Amano, N. Sawaki, I. Akasaki, and Y. Toyoda, *Appl. Phys. Lett.* 48, 353 (1986).
17. K. Dovidenko, S. Oktyabrsky, and J. Narayan, *J. Appl. Phys.* 82, 4296 (1997).
18. B. Heying, X. H. Wu, A. S. Keller, Y. Li, D. Kapolnek, B. P. Keller, S. P. DenBaars, and J. S. Speck, *Appl. Phys. Lett.* 68, 643 (1996).

Conclusion

This concludes the description of the preferred embodiment of the present invention. The following describes some alternative embodiments for accomplishing the present invention.

5 For example, as the inclusions in the description above indicate, there are many modifications and variations of the MOCVD technique and equipment that could be used to grow non-polar $(11\bar{2}0)$ a-plane GaN thin films on $(1\bar{1}02)$ r-plane sapphire substrates. Moreover, different growth conditions may be optimal for different MOCVD reactor designs. Many variations of this process are possible with
10 the variety of reactor designs currently being using in industry and academia. Despite these differences, the growth parameters can most likely be optimized to improve the quality of the films. The most important variables for the MOCVD growth include growth temperature, V/III ratio, precursor flows, and growth pressure.

 In addition to the numerous modifications possible with the MOCVD growth
15 technique, other modifications are possible. For example, the specific crystallographic orientation of the r-plane sapphire substrate might be changed in order to optimize the subsequent epitaxial GaN growth. Further, r-plane sapphire substrates with a particular degree of miscut in a particular crystallographic direction might be optimal for growth.

20 In addition, the nucleation layer deposition is crucial to achieving epitaxial GaN films with smooth growth surfaces and minimal crystalline defects. Other than optimizing the fundamental MOCVD parameters, use of AlN or AlGaIn nucleation layers in place of GaN could prove useful in obtaining high quality a-plane GaN films.

25 Further, although non-polar a-plan GaN thin films are described herein, the same techniques are applicable to non-polar m-plane GaN thin films. Moreover, non-polar InN, AlN, and AlInGaIn thin films could be created instead of GaN thin films.

 Finally, substrates other than sapphire substrate could be employed for non-polar GaN growth. These substrates include silicon carbide, gallium nitride, silicon,

zinc oxide, boron nitride, lithium aluminate, lithium niobate, germanium, aluminum nitride, and lithium gallate.

In summary, the present invention describes the growth of non-polar $(11\bar{2}0)$ a-plane GaN thin films on r-plane $(1\bar{1}02)$ sapphire substrates by employing a low temperature nucleation layer as a buffer layer prior to a high temperature growth of the epitaxial $(11\bar{2}0)$ a-plane GaN films. The epitaxial relationship is $[0001]_{\text{GaN}} \parallel [\bar{1}101]_{\text{sapphire}}$ and $[\bar{1}100]_{\text{GaN}} \parallel [11\bar{2}0]_{\text{sapphire}}$ with the positive GaN c-axis pointing in the same direction as the sapphire c-axis projection on the growth surface.

The foregoing description of one or more embodiments of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in light of the above teaching. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto.

15

WHAT IS CLAIMED IS:

1. A method of growing a non-polar a-plane gallium nitride thin film on an r-plane substrate through metalorganic chemical vapor deposition, comprising:
- 5 (a) annealing the substrate;
- (b) depositing a nitride-based nucleation layer on the substrate;
- (c) growing the non-polar a-plane gallium nitride film on the nucleation layer;
- and
- (d) cooling the non-polar a-plane gallium nitride film under a nitrogen
- 10 overpressure.
2. The method of claim 1, wherein the substrate is an r-plane sapphire substrate.
- 15 3. The method of claim 2, wherein an in-plane orientation of the gallium nitride film with respect to the r-plane substrate is $[0001]_{\text{GaN}} \parallel [\bar{1}101]_{\text{sapphire}}$ and $[\bar{1}100]_{\text{GaN}} \parallel [11\bar{2}0]_{\text{sapphire}}$.
4. The method of claim 1, wherein the substrate is selected from a group
- 20 comprising silicon carbide, gallium nitride, silicon, zinc oxide, boron nitride, lithium aluminate, lithium niobate, germanium, aluminum nitride, and lithium gallate.
5. The method of claim 1, wherein the annealing step (a) comprises a high temperature annealing of the substrate.
- 25 6. The method of claim 1, wherein the depositing step (b) comprises a low temperature deposit of the nitride-based nucleation layer on the substrate.

7. The method of claim 1, wherein the depositing step (b) comprises a low pressure deposit of the nitride-based nucleation layer on the substrate.

8. The method of claim 1, wherein the low temperature depositing
5 conditions comprise approximately 400-900°C and atmospheric pressure.

9. The method of claim 1, wherein the depositing step (b) initiates gallium nitride growth on the r-plane substrate.

10. The method of claim 1, wherein the nucleation layer comprises 1-100
10 nanometers of gallium nitride.

11. The method of claim 1, wherein the growing step (b) comprises a high
temperature growth of the non-polar a-plane gallium nitride film on the nucleation
15 layer.

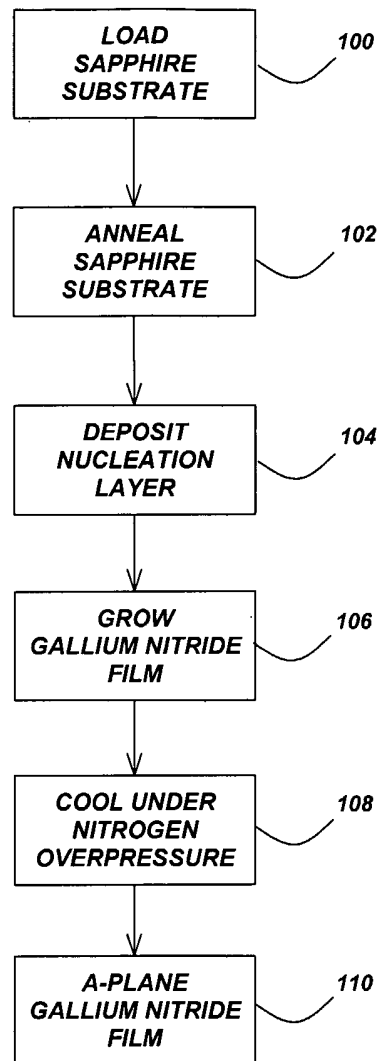
12. The method of claim 11, wherein the high temperature layer is deposited at 0.2 atmospheres or less.

13. The method of claim 11, wherein the high temperature growth
20 conditions comprise approximately 1100°C growth temperature, approximately 0.2 atmosphere or less growth pressure, 30 μmol per minute gallium flow, and 40,000 μmol per minute nitrogen flow.

14. The method of claim 1, wherein the growing step (b) produces the
25 planar gallium nitride film.

15. A device manufactured using the method of claim 1.

1/4

**FIG. 1**

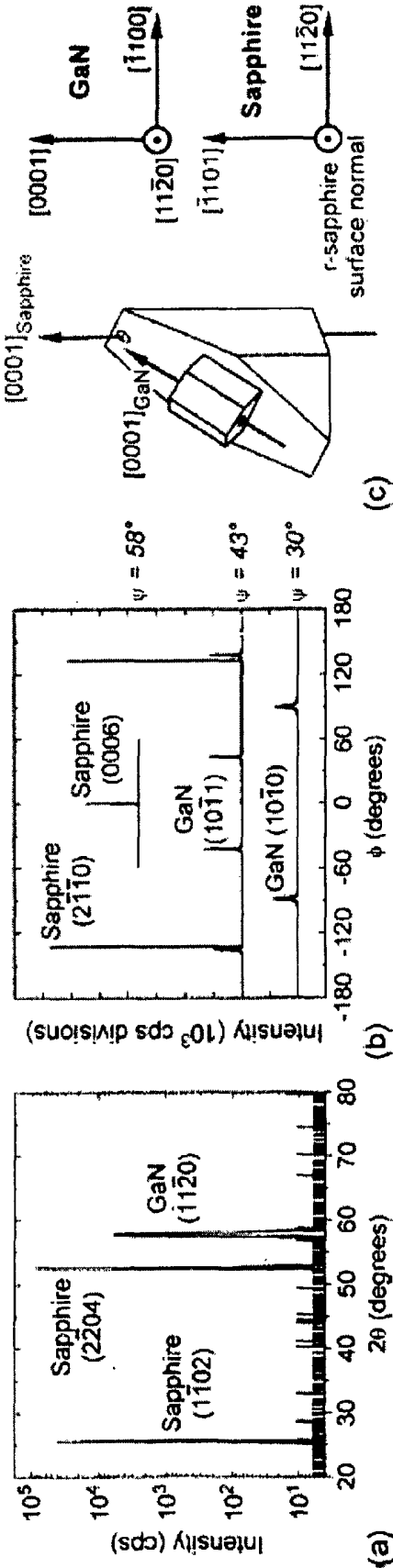


FIG. 2

3/4

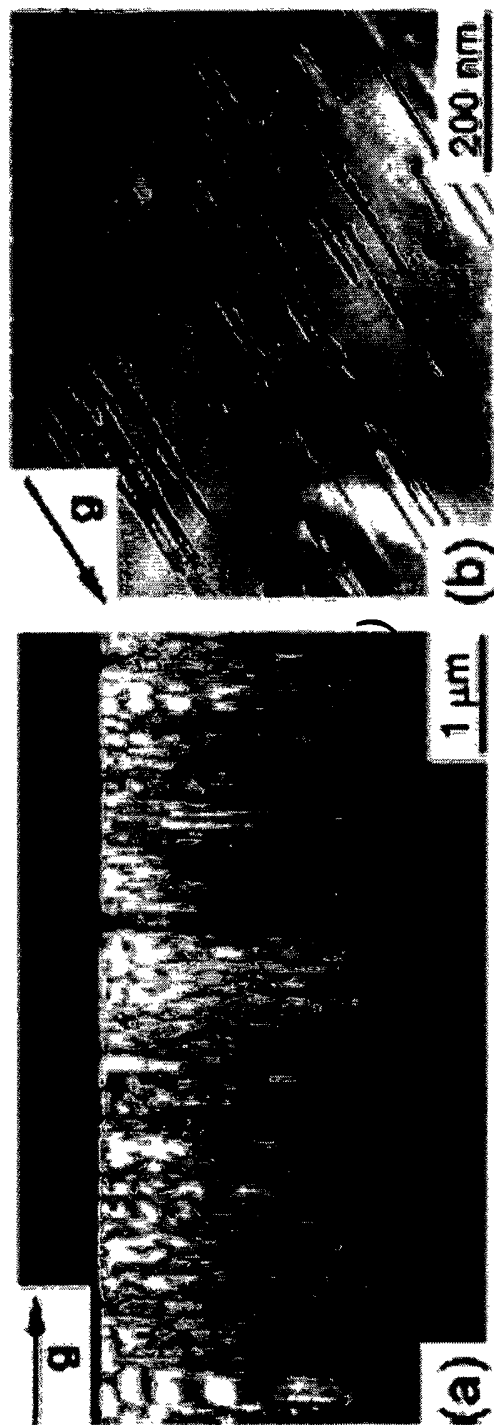
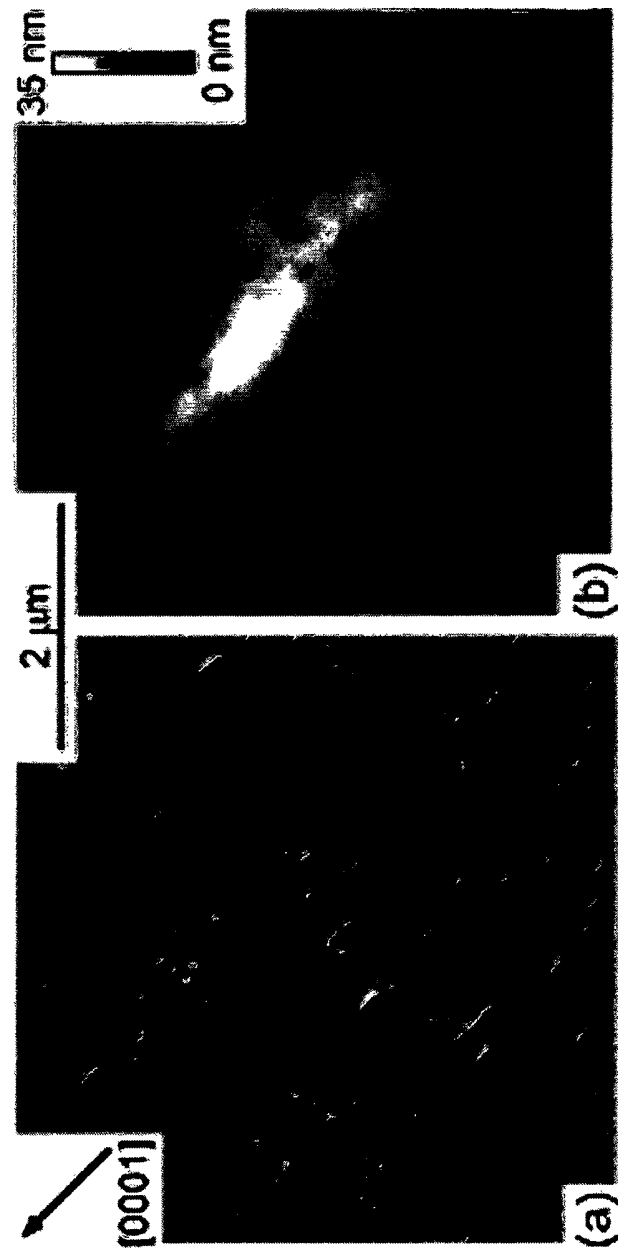


FIG. 3

4/4

**FIG. 4**

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C30B25/02 H01L21/00 H01L21/20 H01L33/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C30B H01L		
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 practical, search terms used) PAJ, EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SASAKI T ET AL: "SUBSTRATE-ORIENTATION DEPENDENCE OF GAN SINGLE-CRYSTAL FILMS GROWN BY METALORGANIC VAPOR-PHASE EPITAXY" JOURNAL OF APPLIED PHYSICS, AMERICAN INSTITUTE OF PHYSICS, NEW YORK, US, vol. 61, no. 7, 1 April 1987 (1987-04-01), pages 2533-2540, XP000820119 ISSN: 0021-8979 cited in the application the whole document --- -/--	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		
T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search 18 August 2003		Date of mailing of the international search report 26/08/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Cook, S

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUN ET AL: "Comparison of the physical properties of GaN thin films deposited on (0001) and (01-12) sapphire substrates" APPLIED PHYSICS LETTERS, vol. 63, no. 7, 1993, pages 973-975, XP002251480 NEW YORK US cited in the application the whole document ---	1
T	CRAVEN ET AL: "Structural characterization of nonpolar (11-20) a-plane GaN thin films grown on (1-102) r-plane sapphire" APPLIED PHYSICS LETTERS, vol. 81, no. 3, 15 July 2002 (2002-07-15), pages 469-471, XP002250684 NEW YORK US cited in the application the whole document ---	1-15
A	EP 0 942 459 A (NICHIA KAGAKU KOGYO KK) 15 September 1999 (1999-09-15) claims 1,48-50,59; figures 3,5A; example 4 ---	1
A	US 2001/029086 A1 (IMAFUJI OSAMU ET AL) 11 October 2001 (2001-10-11) paragraph '0182! ---	1
A	GRZEGORY I ET AL: "Seeded growth of GaN at high N2 pressure on (0001) polar surfaces of GaN single crystalline substrates" MATERIALS SCIENCE IN SEMICONDUCTOR PROCESSING, ELSEVIER SCIENCE PUBLISHERS B.V., BARKING, UK, vol. 4, no. 6, December 2001 (2001-12), pages 535-541, XP004345737 ISSN: 1369-8001 -----	

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0942459	A	15-09-1999	EP 0942459 A1	15-09-1999
			US 6153010 A	28-11-2000
			CA 2258080 A1	22-10-1998
			JP 11191657 A	13-07-1999
			WO 9847170 A1	22-10-1998
			KR 2000016589 A	25-03-2000
			TW 406445 B	21-09-2000
			US 2003037722 A1	27-02-2003
			US 2002046693 A1	25-04-2002
			JP 11191637 A	13-07-1999
			JP 2003101159 A	04-04-2003
			JP 11191659 A	13-07-1999
			JP 11219910 A	10-08-1999
<hr/>				
US 2001029086	A1	11-10-2001	JP 2001345266 A	14-12-2001
<hr/>				