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(54) **LOW DEFECT GROUP III NITRIDE FILMS
USEFUL FOR ELECTRONIC AND
OPTOELECTRONIC DEVICES AND
METHODS FOR MAKING THE SAME**

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(57) **ABSTRACT**

In a method for making a low-defect single-crystal GaN film, an epitaxial nitride layer is deposited on a substrate. A first GaN layer is grown on the epitaxial nitride layer by HVPE under a growth condition that promotes the formation of pits, wherein after growing the first GaN layer the GaN film surface morphology is rough and pitted. A second GaN layer is grown on the first GaN layer to form a GaN film on the substrate. The second GaN layer is grown by HVPE under a growth condition that promotes filling of the pits, and after growing the second GaN layer the GaN film surface morphology is essentially pit-free. A GaN film having a characteristic dimension of about 2 inches or greater, and a thickness normal ranging from approximately 10 to approximately 250 microns, includes a pit-free surface, the threading dislocation density being less than $1 \times 10^8 \text{ cm}^{-2}$.

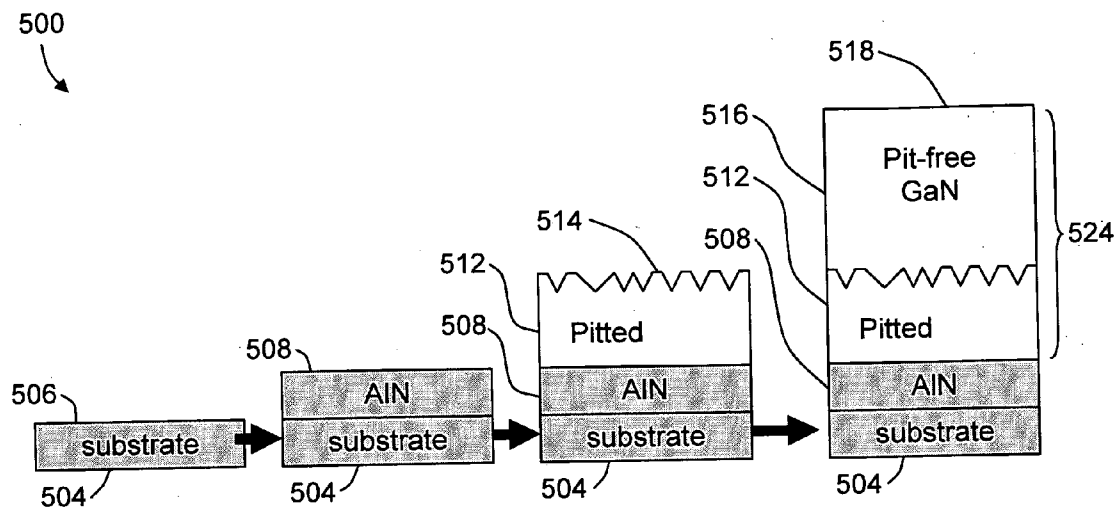
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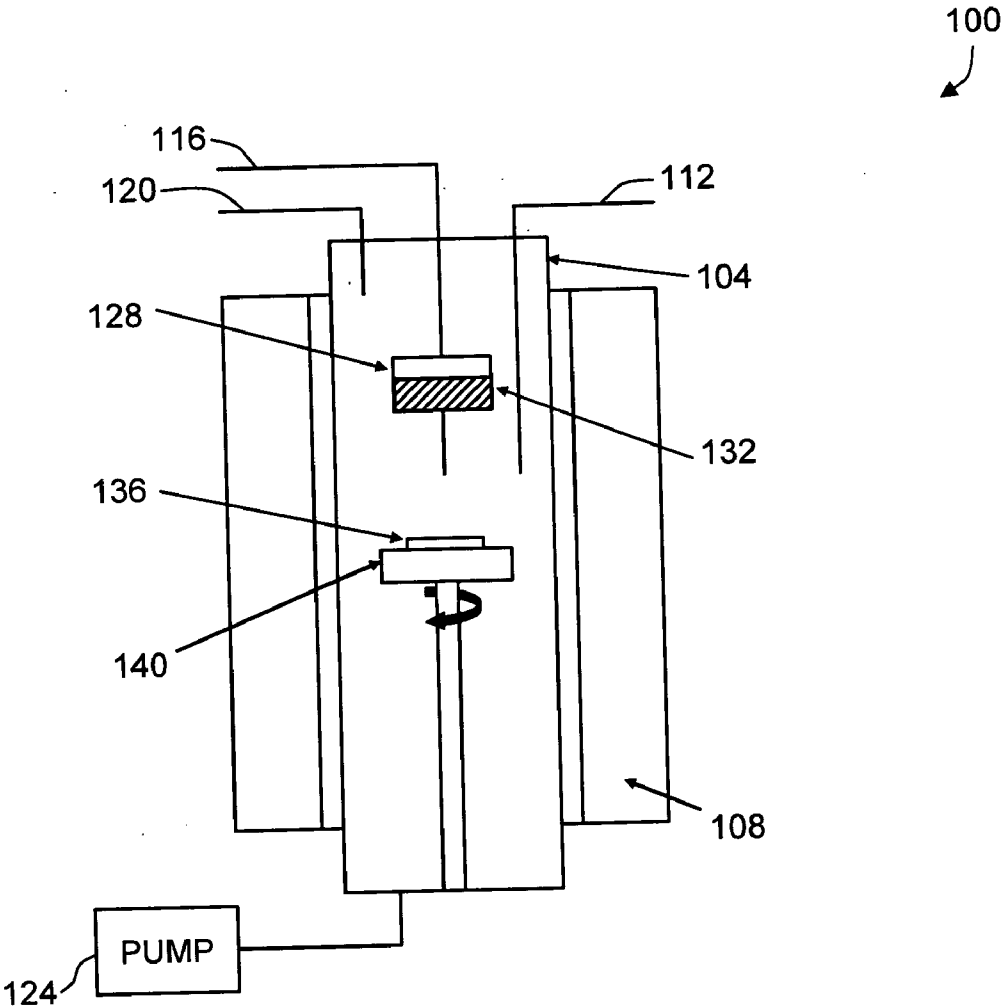


Fig. 1

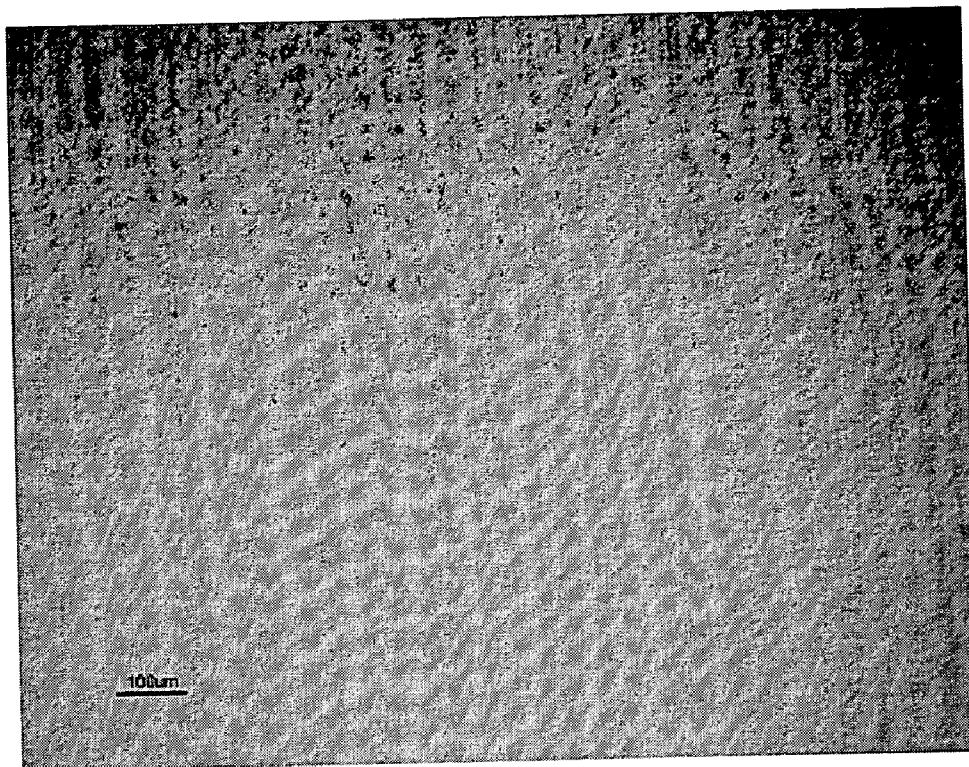


Fig. 2

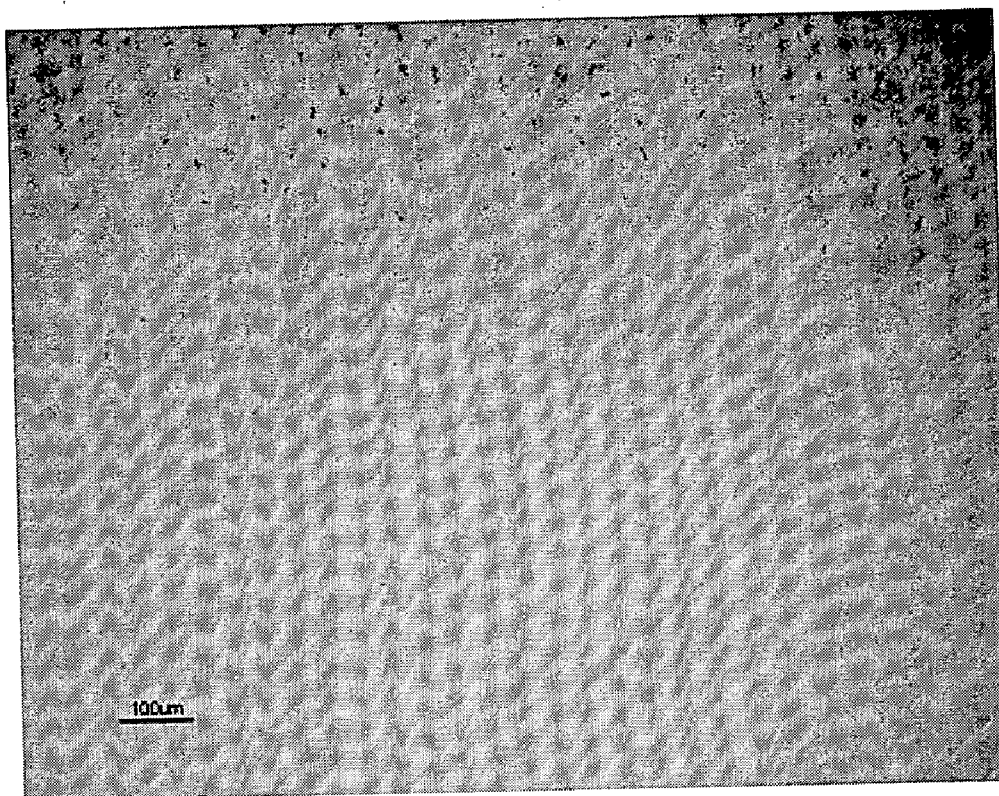


Fig. 3

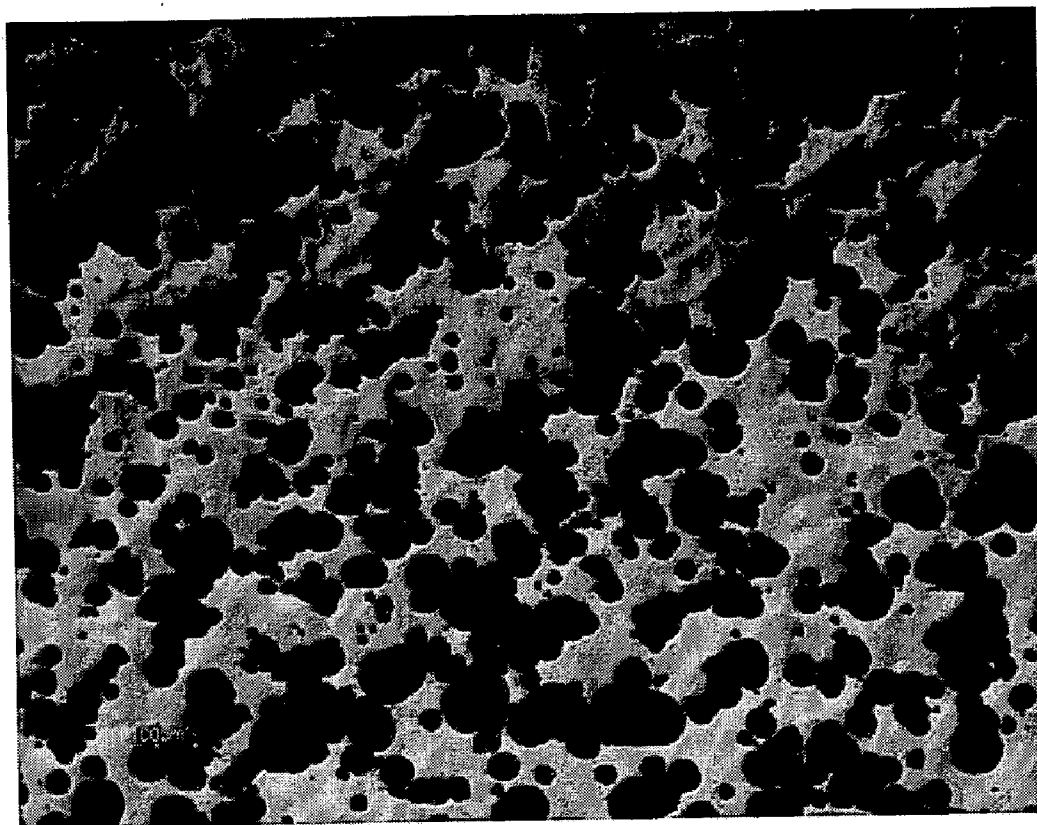


Fig. 4

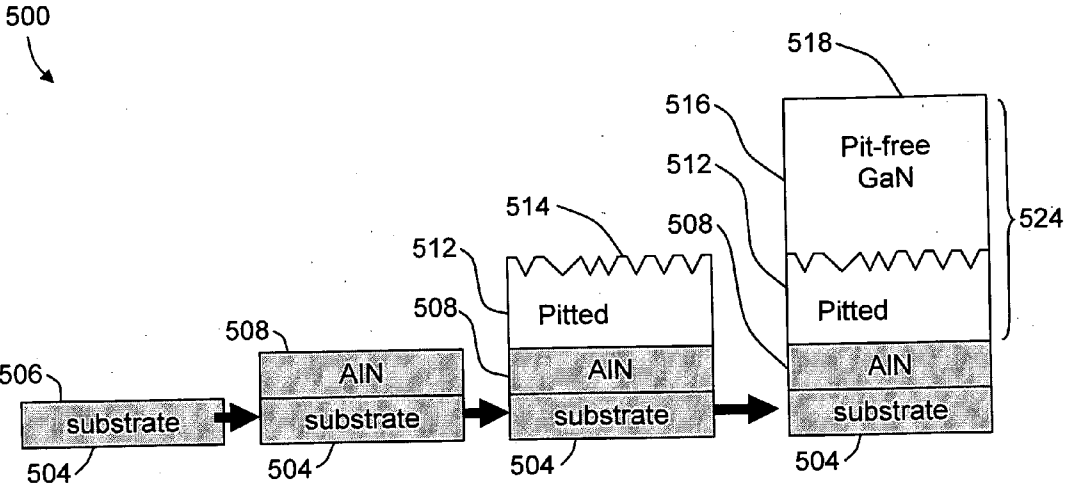


Fig. 5

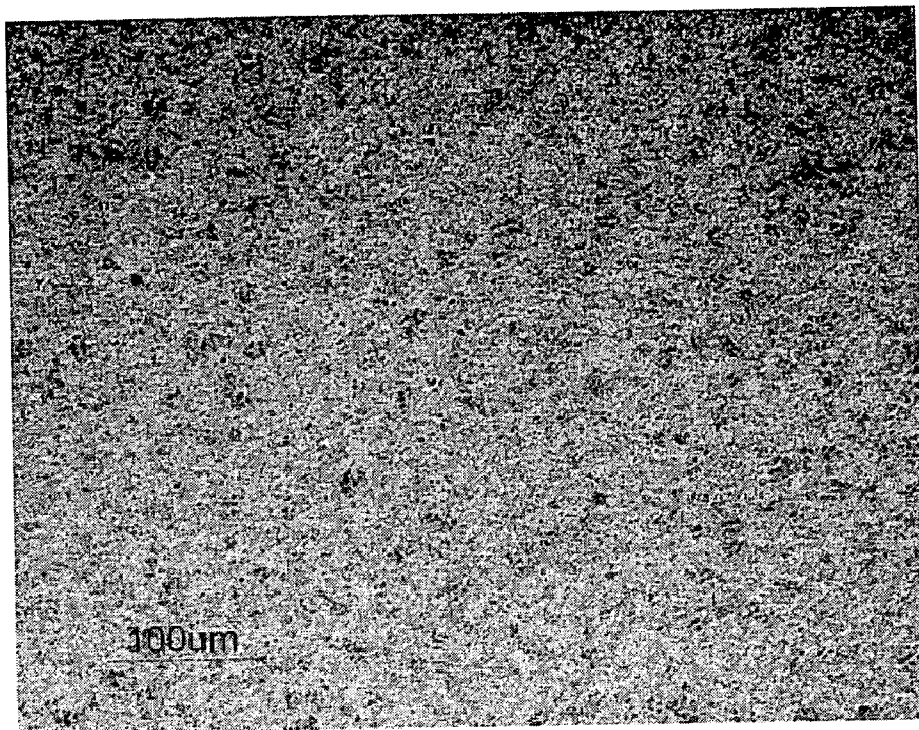


Fig. 6

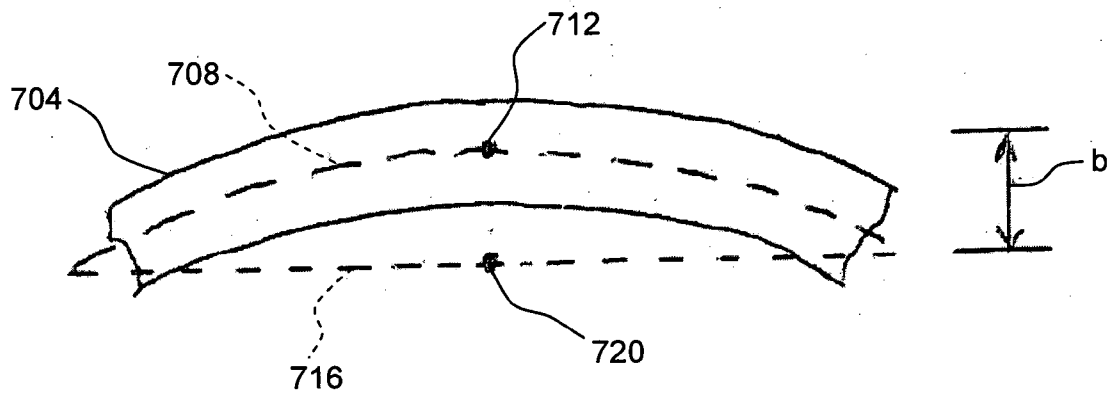


Fig. 7

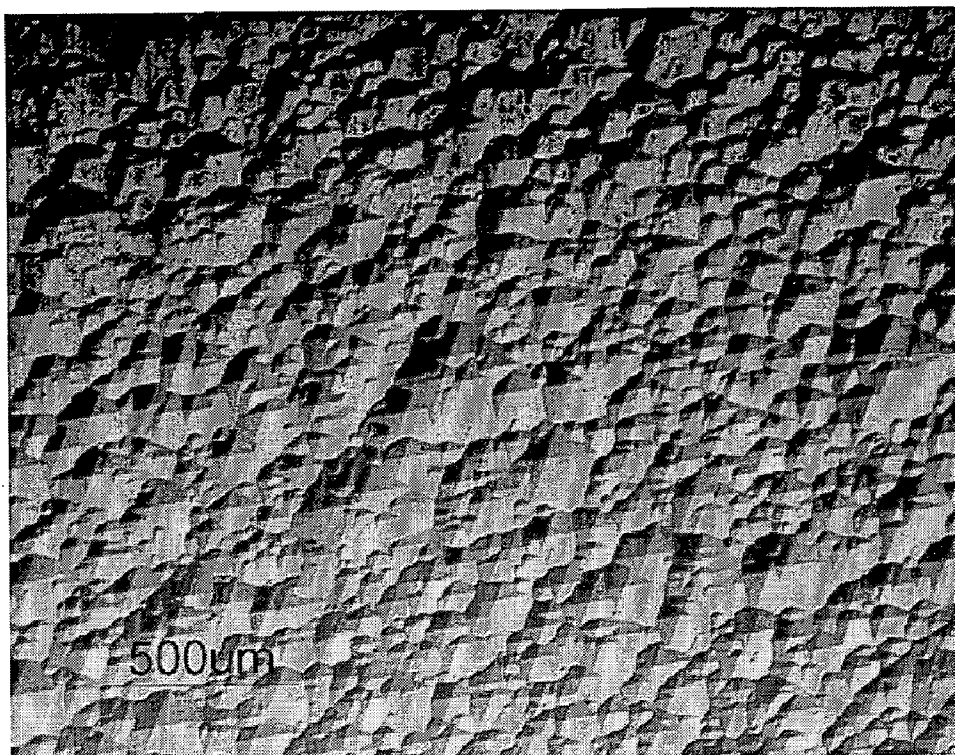


Fig. 8

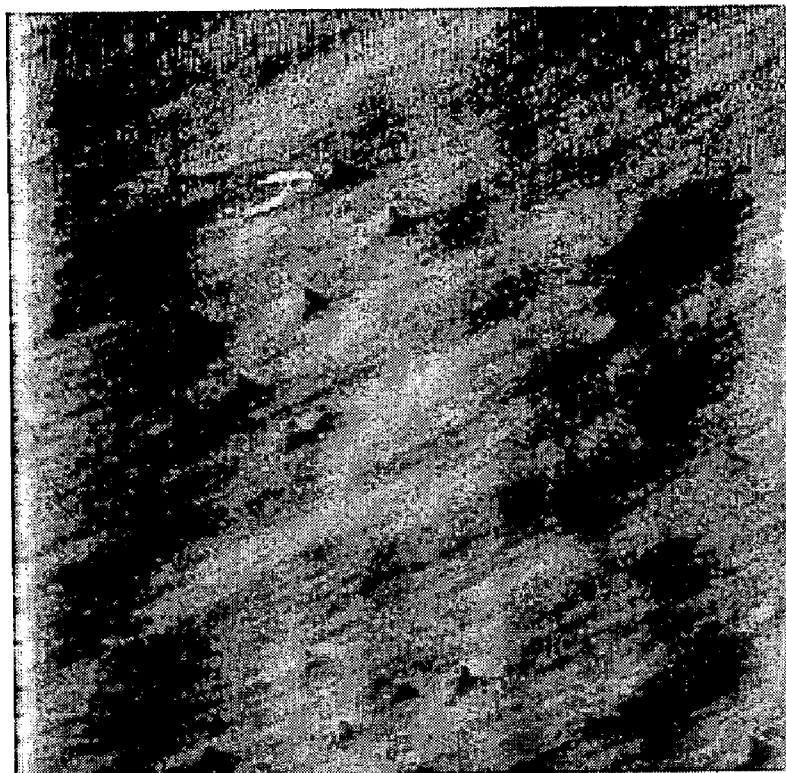


Fig. 9

**LOW DEFECT GROUP III NITRIDE FILMS
USEFUL FOR ELECTRONIC AND
OPTOELECTRONIC DEVICES AND METHODS
FOR MAKING THE SAME**

CROSS-REFERENCE TO RELATED
APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 60/749,728, filed Dec. 12, 2005, titled "Bulk Gallium Nitride Crystals and Method of Making the Same;" U.S. Provisional Patent Application Ser. No. 60/750,982, filed Dec. 16, 2005, titled "Method of Producing Freestanding Gallium Nitride by Self-Separation;" U.S. Provisional Patent Application Ser. No. 60/810,537, filed Jun. 2, 2006, titled "Low Defect GaN Films Useful for Electronic and Optoelectronic Devices and Method of Making the Same;" U.S. Provisional Patent Application Ser. No. 60/843,036, filed Sep. 8, 2006, titled "Methods for Making Inclusion-Free Uniform Semi-Insulating Gallium Nitride Substrate;" and U.S. Provisional Patent Application Ser. No. 60/847,855, filed Sep. 28, 2006, titled "Method of Producing Single Crystal Gallium Nitride Substrates by HVPE Method Incorporating a Polycrystalline Layer for Yield Enhancement," the contents of which are incorporated by reference herein in their entireties.

BACKGROUND

[0002] 1. Field of the Invention

[0003] This invention relates to low-defect density, device-quality gallium nitride (Al, Ga, In)N films useful for producing electronic and optoelectronic devices, such as high electron mobility transistors (HEMTs), heterojunction bipolar transistors (HBTs), light emitting diodes (blue, UV and white LEDs), and laser diodes (LDs). The invention also relates to methods for producing such GaN films.

[0004] 2. Description of the Related Art

[0005] Group III-V nitride compounds such as aluminum nitride (AlN), gallium nitride (GaN), indium nitride (InN), and alloys such as AlGaIn, InGaIn, and AlGaInN, are direct bandgap semiconductors with bandgap energy ranging from about 0.6 eV for InN to about 6.2 eV for AlN. These materials may be employed to produce light emitting devices such as LEDs and LDs in short wavelength in the green, blue and ultraviolet (UV) spectra. Blue and violet laser diodes may be used for reading data from and writing data to high-density optical data storage discs, such as those used by Blu-Ray and HD-DVD systems. By using proper color conversion with phosphors, blue and UV light emitting diodes may be made to emit white light, which may be used for energy efficient solid-state light sources. Alloys with higher bandgaps can be used for UV photodetectors that are insensitive to solar radiation. The material properties of the III-V nitride compounds are also suitable for fabrication of electronic devices that can be operated at higher temperature, or higher power, and higher frequency than conventional devices based on silicon (Si) or gallium arsenide (GaAs).

[0006] Most of the III-V nitride devices are grown on foreign substrates such as sapphire (Al_2O_3) and silicon carbide (SiC) because of the lack of available low-cost, high-quality, large-area native substrates such as GaN sub-

strates. Blue LEDs are mostly grown on insulating sapphire substrates or semi-conducting silicon carbide substrates using a metal-organic chemical vapor deposition (MOCVD) process.

[0007] The MOCVD process is a slow growth rate process with a growth rate of a few microns per hour. In a typical GaN-based device growth process, a low-temperature buffer layer of GaN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x=0-1$) is first grown on a foreign substrate (e.g., sapphire or silicon carbide), followed by the growth of a few microns of GaN. The active device layer, such as quantum well structures for LEDs, is subsequently grown. For example, U.S. Pat. No. 5,563,422 to S. Nakamura et al. describes a GaN-based device grown by an MOCVD process. A thin GaN nucleation layer of about 10 nanometers is first deposited on a sapphire substrate at a low temperature of 500-600° C. The GaN nucleation layer is annealed at high temperature to recrystallize the GaN, and epitaxial GaN film is grown at higher temperature (approximately 1000-1200° C.).

[0008] Because of the lattice mismatch between gallium nitride and the non-native substrate, there is a large number of crystal defects in the GaN film and active device layer. The defect density in the GaN nucleation layer is thought to be on the order of 10^{11} cm^{-2} or greater, and in the subsequently grown GaN layer and active device layer, the typical density of crystal defects, in particular, the threading dislocation density, is on the order of 10^9 - 10^{10} cm^{-2} or greater in typical GaN-based LEDs. Despite the high defect density of LEDs grown on these substrates, commercial low-power blue/white LEDs have long lifetimes suitable for some applications.

[0009] Group III-V nitride-based laser diodes, however, show a remarkable dependence of lifetime on the crystal defect density. The lifetime of these LDs dramatically decreases with the increase of the dislocation density (see, for example, "Structural defects related issues of GaN-based laser diodes," S. Tomiya et al., MRS Symposium Proceedings, Vol. 831, p. 3-13, 2005). Low-defect density single-crystal gallium nitride is needed for the long lifetime (>10,000 hours) nitride laser diodes. For LEDs based on an AlGaIn active layer operating at the deeper UV range, it is also found that dislocation density has a detrimental effect on the performance and lifetime of the devices. For LEDs operating at higher power levels, it is also desirable to have a lower defect density GaN layer.

[0010] There are several growth methods that may possibly be performed to reduce the defect density of the gallium nitride film. One common approach in MOCVD growth of gallium nitride is epitaxial lateral overgrowth (ELOG) and its variations. In an ELOG GaN growth process, a GaN film is first grown by a MOCVD method with the 2-step process (low-temperature buffer and high-temperature growth). A dielectric layer such as silicon oxide or silicon nitride is deposited on the first GaN film. The dielectric layer is patterned with a photolithographic method and etched so that portions of GaN surface are exposed and portions of the GaN film are still covered with the dielectric mask layer. The patterned GaN film is reloaded into the MOCVD reactor and growth is re-commenced. The growth condition is chosen such that the second GaN layer can only be grown on the exposed GaN surface, but not directly on the masked area. When the thickness of the second GaN layer is thicker than

the dielectric layer, GaN can grow not only along the original c direction, but also along the sidewalls of the GaN growing out of the exposed area and gradually covering the dielectric mask. At the end of the growth, the dielectric mask will be completely covered by the GaN film and the GaN film overall is quite smooth. However, the distribution of the threading dislocation density is not uniform. Since the dislocation density of the first GaN layer is quite high, the defect density is also high in the area of the second GaN layer grown directly on the exposed first GaN layer. In comparison, the defect density is much reduced in the area above the dielectric mask area where the second GaN layer was grown laterally in the direction parallel to the surface. The defect density is still high in the area where the second GaN layer was grown directly on the first GaN layer and in the area where the lateral grown GaN coalesced. Multiple ELOG processes can be used to further reduce the defect density by patterning a second dielectric mask covering the high defect density areas of the first ELOG GaN film, and growing GaN film in the ELOG condition that yields a coalesced second ELOG film.

[0011] The manufacturing cost of the prior-art low defect density GaN film based on MOCVD is high due to multiple growth and photolithographic steps. The high cost of the film also increases the overall manufacturing cost of end products such as UV LEDs.

[0012] Therefore, there is still a compelling need in the art for a low-cost method of producing high-quality, low defect density GaN films that are suitable for electronic and optoelectronic devices to be built on.

SUMMARY

[0013] The present invention generally relates to high-quality gallium nitride (Al, Ga, In)N films (articles, substrates, layers, etc.) and methods for making the same.

[0014] According to one implementation, a method for making a low-defect single-crystal gallium nitride (GaN) film is provided. An epitaxial aluminum nitride (AlN) layer is deposited on a substrate. A first epitaxial GaN layer is grown on the AlN layer by HVPE under a growth condition that promotes the formation of pits, wherein after growing the first GaN layer the GaN film surface morphology is rough and pitted. A second epitaxial GaN layer is grown on the first GaN layer to form a GaN film on the substrate. The second GaN layer is grown by HVPE under a growth condition that promotes filling of the pits, and after growing the second GaN layer the GaN film surface morphology is essentially pit-free.

[0015] According to another implementation, the GaN growth condition for growing the first GaN layer is selected from the group consisting of a higher growth rate than during growth of the second GaN layer, a lower growth temperature than during growth of the second GaN layer, a higher ammonia flow than during growth of the second GaN layer, and two or more of the foregoing.

[0016] According to another implementation, a low-defect single-crystal GaN film produced according to any of the above methods is provided.

[0017] According to another implementation, a low-defect single-crystal GaN film is provided. The GaN film has a characteristic dimension of about 2 inches or greater, and a

thickness normal to the characteristic dimension ranging from approximately 10 to approximately 250 microns. The GaN film includes a pit-free surface. The threading dislocation density on the GaN film surface being less than $1 \times 10^8 \text{ cm}^{-2}$.

[0018] According to another implementation, low-defect single-crystal gallium nitride (GaN) on substrate structure is provided. The structure includes a substrate, an epitaxial aluminum nitride (AlN) layer on the substrate, and a GaN film on the substrate. The GaN film includes a first epitaxial GaN growth layer and a second epitaxial GaN growth layer. The first epitaxial GaN layer is grown on the AlN layer under a growth condition that promotes the formation of pits, and after growing the first GaN layer the GaN film surface morphology is rough and pitted. The second epitaxial GaN is grown on the first GaN layer by HVPE under a growth condition that promotes filling of the pits formed, and after growing the second GaN layer the GaN film surface morphology is essentially pit-free.

[0019] According to any of the above implementations, the threading dislocation density on the GaN film surface is minimal. In one example, the threading dislocation density on the surface of the GaN film may be less than $1 \times 10^8 \text{ cm}^{-2}$, in another example less than $5 \times 10^7 \text{ cm}^{-2}$, in another example less than $1 \times 10^7 \text{ cm}^{-2}$, and in another example less than $5 \times 10^6 \text{ cm}^{-2}$.

[0020] According to any of the above implementations, the amount of bowing the GaN film on an underlying substrate is minimal. In one example, the bow of the GaN film may be less than about 200 microns. In another example, the bow of the GaN film may be less than about 100 microns. In another example, the bow of the GaN film may be less than about 50 microns. In another example, the bow of the GaN film may be less than about 25 microns.

[0021] According to any of the above implementations, the surface of the GaN film may have a root-mean square (RMS) surface roughness of about 0.5 nm or less.

[0022] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 is a schematic view of a vertical HVPE reactor.

[0024] FIG. 2 is an optical micrograph at 50× magnification of the surface of a GaN film grown on an AlN-coated sapphire substrate under a typical HVPE GaN growth condition. The GaN film thickness was approximately 1 micron.

[0025] FIG. 3 is an optical micrograph at 50× magnification of a GaN film grown on an AlN-coated sapphire substrate under the same condition as the film shown in FIG. 2, but to a thickness of approximately 5 microns. Microcracking of the film is visible.

[0026] FIG. 4 is an optical micrograph at 50× magnification of a pitted GaN film, approximately 110 microns thick, grown on AlN-coated sapphire substrate under a moderate NH_3 partial pressure growth condition.

[0027] FIG. 5 is a schematic illustration of an example of a growth process of the present invention.

[0028] FIG. 6 is an optical micrograph at 200× magnification of the surface of a GaN layer at the end of a growth step in which the surface is pitted, according to one implementation of the present invention.

[0029] FIG. 7 is a cross-sectional view of a bowed wafer or layer of material.

[0030] FIG. 8 is an optical micrograph at 50× magnification of the surface of an as-grown 60-micron GaN film on sapphire substrate, according to one implementation of the present invention.

[0031] FIG. 9 is a 10×10-micron AFM scan of a 60-micron thick GaN film on sapphire, grown according to one implementation of the present invention.

DETAILED DESCRIPTION

[0032] Throughout the disclosure, unless otherwise specified, certain terms are used as follows. “Single crystalline film” or “single crystal” means a crystalline structure that can be characterized with x-ray rocking curve measurement. The narrower the peak of the rocking curve, the better the crystal quality. “Single crystal” does not necessarily mean that the whole crystal is a single grain; it may contain many crystalline grains with orientation more or less aligned. “Polycrystalline film” or “polycrystal” means that a crystal has many grains whose crystal orientations are randomly distributed. An X-ray rocking curve measurement of a polycrystalline film does not exhibit a peak. “Microcracks” are a cluster of localized cracks with high density of cracks. The distance between the parallel cracks in the microcrack cluster is typically less than 100 microns. “Growth cracks” are the cracks formed during crystal growth. “Cool down cracks” or “thermal cracks” are the cracks formed after the crystal growth and during the cooling of the crystal from the growth temperature to ambient or room temperature. “Pits” are typically inverse pyramidal pits on the crystal surface. “Pit-free surface” is a surface essentially having no pits on its surface. “Pitted surface morphology” means a surface having a substantial amount of pits on its surface. “Faceted surface morphology” means that a single crystal film surface is completely covered with pits so that the sides of the pits become the surface itself and the surface appears faceted. “Smooth surface morphology” means that a surface is specular and has no visual defects (such as pits). “Nucleation layer” or “template layer” in some implementations may be the layer first grown on a substrate. “V:III ratio” in some implementations is the ratio of the ammonia flow to the HCl flow used during a hydride vapor phase epitaxy GaN growth process. “Ammonia partial pressure” is calculated according to the ammonia flow, the total gas flow into a reactor, and the reactor pressure. “Growth surface” or “growing surface” or “growth front” is the surface of the GaN crystal during the instance of the growth.

[0033] For purposes of the present disclosure, it will be understood that when a layer (or film, region, substrate, component, device, or the like) is referred to as being “on” or “over” another layer, that layer may be directly or actually on (or over) the other layer or, alternatively, intervening layers (e.g., buffer layers, transition layers, interlayers, sacrificial layers, etch-stop layers, masks, electrodes, interconnects, contacts, or the like) may also be present. A layer that is “directly on” another layer means that no intervening layer is present, unless otherwise indicated. It will also be

understood that when a layer is referred to as being “on” (or “over”) another layer, that layer may cover the entire surface of the other layer or only a portion of the other layer. It will be further understood that terms such as “formed on” or “disposed on” are not intended to introduce any limitations relating to particular methods of material transport, deposition, fabrication, surface treatment, or physical, chemical, or ionic bonding or interaction.

[0034] Unless otherwise indicated, terms such as “gallium nitride” and “GaN” are intended to describe binary, ternary, and quaternary Group III nitride-based compounds such as, for example, gallium nitride, indium nitride, aluminum nitride, aluminum gallium nitride, indium gallium nitride, indium aluminum nitride, and aluminum indium gallium nitride, and alloys, mixtures, or combinations of the foregoing, with or without added dopants, impurities or trace components, as well as all possible crystalline structures and morphologies, and any derivatives or modified compositions of the foregoing. Unless otherwise indicated, no limitation is placed on the stoichiometries of these compounds.

[0035] Single-crystal GaN films can be grown on sapphire substrates with various vapor phase growth techniques, such as molecular beam epitaxy (MBE), metal-organic vapor phase epitaxy (MOVPE), and hydride vapor phase epitaxy (HVPE). In the MBE and MOVPE growth of GaN films on sapphire, a low-temperature buffer layer is typically needed to grow high-quality GaN film. It is not clear whether a buffer layer is needed for HVPE GaN growth on sapphire. Lee in U.S. Pat. No. 6,528,394 discloses a specific method of pre-treatment for growing GaN on sapphire using HVPE. The pre-treatment involves etching sapphire with a gas mixture of hydrochloric acid (HCl) and ammonia (NH₃), as well as nitridation of the sapphire substrate. Molnar in U.S. Pat. No. 6,086,673 discloses the use of a zinc oxide (ZnO) pretreatment layer that was further reacted in the gaseous environment of HCl and/or NH₃. After this treatment of sapphire substrate, single-crystal GaN film is then grown by HVPE. On the other hand, Vaudo et al in U.S. Pat. No. 6,440,823 discloses the growth of a low defect density GaN layer on sapphire by the HVPE method, without using any buffer layers or nucleation layers.

[0036] Since teachings in the prior art regarding sapphire substrate treatment or initiation prior to HVPE GaN growth are in conflict, we systematically investigated the growth of gallium nitride film on sapphire using an HVPE process. Vertical HVPE reactors were used for the investigation. FIG. 1 schematically illustrates an example of a vertical HVPE reactor 100. The HVPE reactor 100 includes a quartz reactor tube 104 that is heated by a multi-zone furnace 108. The reactor tube 104 is connected to gas inlets 112, 116, and 120 for introducing reactants, carrier gases, and diluting gases. The reactor tube 104 is also connected to a pump and exhaust system 124. In some implementations, inside the reactor 100, gaseous hydrochloric acid (HCl) is flowed through a vessel 128 containing gallium metal 132, which is at a temperature of, for example, about 850° C. The hydrochloric acid reacts with the gallium metal 132, forming gaseous GaCl, which is transported by a carrier gas, such as nitrogen, to the deposition zone in the reactor tube 104. Ammonia (NH₃) and an inert diluent gas, such as nitrogen, are also flowed to the deposition zone where GaN crystals are deposited. The reactor 100 is designed such that the mixing of GaCl and NH₃ does not occur near the gas outlets,

ensuring no deposition of GaN on the outlets of GaCl and NH₃ and enabling long-term stability of gas flow patterns. Epi-ready c-plane sapphire substrates or other suitable substrates **136** may be used. The substrate **136** is placed on a rotating platter **140** and heated to a temperature of, for example, 900-1100° C.

[0037] A typical deposition run process is as follows: (1) a substrate **136** is placed on the platter **140**, (2) the reactor **100** is sealed, (3) the reactor **100** is evacuated and purged with high-purity nitrogen to remove any impurities from the system, (4) the platter **140** with the substrate **136** is raised to the deposition zone, (5) the platter temperature is controlled at the desired deposition temperature, (6) ammonia is flowed into the reactor **100**, (7) HCl is flowed to the reactor **100** to start the GaN deposition, (8) deposition proceeds according to a predetermined recipe for a predetermined time, (9) the HCl and NH₃ gas flows are stopped, (10) the platter **140** is lowered and the grown crystal is gradually cooled down, and (11) the grown crystal is removed for characterization and further processing.

[0038] After systematically investigating the HVPE growth of GaN on sapphire substrates, we uncovered several issues that were not disclosed in the prior art, namely, irreproducible nucleation of single crystal GaN films on untreated sapphire substrates, and microcracking of single crystalline GaN films.

[0039] First, we grew various HVPE GaN films directly on sapphire substrates without any buffer layer or pretreatment under the conditions taught by the prior art, i.e., a growth temperature of about 950-1050° C., V:III ratio (i.e., NH₃/HCl) of about 10-50, and a growth rate of about 100 microns per hour. The bare sapphire substrate was heated up to the growth temperature, ammonia flow was turned on first to fill the reactor to a pre-determined partial pressure and HCl flow was turned on to initiate the growth. The GaN film grown directly on the bare sapphire substrate was not smooth. After analyzing the grown GaN films with an x-ray rocking curve and optical microscope, we determined that the GaN films grown directly on bare sapphire substrates were not single-crystalline films. In fact, they were polycrystalline GaN. We wish not to be bound by any particular theory regarding the various results of HVPE GaN crystal growth on sapphire, but the discrepancy in the various prior-art work and our own work may be related to particular reactor configurations or surface treatments. The prior art did not teach a reproducible method to grow single crystal GaN films on sapphire substrate by HVPE.

[0040] There is a large lattice mismatch between sapphire and gallium nitride. Furthermore, c-plane GaN is a polar crystal, i.e., one face is terminated with gallium and the opposite face of the crystal is terminated with nitrogen. On the other hand, sapphire is not a polar crystal; the c-plane of sapphire is terminated with oxygen on both faces. In other GaN thin-film deposition techniques such as molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD), a thin buffer layer is required for the high-quality single-crystalline GaN growth. The buffer layer may be an AlN layer (S. Yoshida et al., Appl. Phys. Lett., 42, 427 (1983); H. Amano et al., Appl. Phys. Lett., 48, 353 (1986)) or a GaN layer grown at low temperature (S. Nakamura, Jpn. J. Appl. Phys., 30, L1705 (1991)). Lee in

U.S. Pat. No. 6,528,394 postulated the formation of a thin AlN layer on the sapphire surface by the pre-treatment step prior to HVPE GaN growth.

[0041] U.S. Pat. No. 6,784,085, the entire contents of which are incorporated into the present disclosure, discloses a high-temperature reactive sputtering method for growing high-quality AlN film on sapphire substrates. Using this method, we coated sapphire substrates with AlN for use as substrates for HVPE GaN growth.

[0042] High-quality GaN thin films were successfully and reproducibly grown on the AlN-coated sapphire substrate. We first grew a thin layer of AlN film on a sapphire substrate by sputtering using the method disclosed in U.S. Pat. No. 6,784,085. The typical thickness of the AlN layer was approximately 0.5-2 microns. X-ray rocking curve measurement indicated the AlN film was an epitaxial and single-crystalline film with (0002) rocking curve full width at half maximum (FWHM) of 50 arcsec. The AlN-coated sapphire substrate was loaded into the HVPE reactor and a GaN film was grown using the aforementioned procedure. The growth rate was about 60 microns per hour, the GaCl partial pressure was about 2.97 Torr, the NH₃ partial pressure was about 44.6 Torr, the V:III ratio was about 15, and the growth temperature was about 950° C. as measured with a thermocouple under the platter. The growth time was 1 minute. The GaN film grown was transparent with a smooth, specular surface. FIG. 2 shows an optical micrograph of the surface of the GaN film. FIG. 2 shows a typical smooth surface morphology for an HVPE GaN film with some hillock features. X-ray rocking curve measurements confirm the single-crystalline nature of the GaN film, with a FWHM value of 297 arcsec.

[0043] After developing a nucleation process for GaN single crystalline films on AlN sputter-coated sapphire substrates, we investigated the growth of thicker GaN films. We discovered a problem, namely, microcracking in the GaN films. The HVPE growth conditions were chosen to produce a smooth GaN surface. FIG. 3 shows an optical micrograph of thin GaN film, approximately 5 microns thick on an AlN-coated sapphire substrate, grown under the same conditions as the film shown in FIG. 2. The surface exhibits a typical smooth HVPE GaN morphology with hillock features. However, microcracks in the GaN film are apparent. The sapphire substrate remains intact without any cracking in this case.

[0044] Because of the difference between the coefficients of thermal expansion of the sapphire substrate and the GaN film, thermal stress builds up when the film cools down from the typical growth temperature of about 1000° C. to ambient room temperature. As discussed in open literature (for example, E. V. Etzkom and D. R. Clarke, "Cracking of GaN Films," J. Appl. Phys., 89 (2001) 1025), sapphire substrate shrinks faster than GaN film during cool down, causing a compressive stress in the GaN film due to this thermal expansion mismatch. The compressive thermal stress in the GaN film should not cause microcracking in the GaN film during cool down. Therefore, the microcracks must be already formed during the GaN growth and prior to cool down.

[0045] The microcracking of the GaN film during the growth suggests a tensile stress in the GaN film during the growth. We wish not be bound by any particular theory

regarding the origin of microcracking during GaN growth. However, the tensile stress may be related to the AlN layer employed in the study, or may be related to the HVPE growth condition used, or may be universal to the vapor phase GaN growth in general. While cracking is noted in some instances, most prior-art literature in HVPE GaN growth does not disclose the formation of microcracks in GaN film during growth. The prior art also does not teach how to eliminate the microcracks during the HVPE GaN growth.

[0046] In order to eliminate the microcracks formed during the HVPE GaN growth, we systematically investigated GaN growth on the AlN-coated sapphire under various growth conditions by varying growth parameters, such as GaCl flow or partial pressure (which may be determined by the flow of hydrochloric acid (HCl)), NH₃ flow or partial pressure, growth temperature, and associated variables such as growth rate and V:III ratio (e.g., NH₃/HCl ratio). In this example, the V:III ratio is the ratio of the NH₃/HCl flow. The growth rate is typically proportional to GaCl partial pressure, which is directly related to the HCl flow. We found that the surface morphology of the GaN film varies substantially with the growth temperature, growth rate and ammonia partial pressure (or V:III ratio). At a constant growth temperature and GaCl partial pressure, increasing NH₃ partial pressure dramatically alters behavior of microcracking and surface morphology. For a constant growth time (similar film thickness, about 100 microns), the HVPE GaN surface morphology gradually changes from a smooth, hillock morphology with microcracks at low NH₃ partial pressure, to a surface covered with pits at moderately high NH₃ partial pressure, and eventually to polycrystalline material at high NH₃ partial pressure. When the GaN film is covered with pits, the microcracks formed during the growth are also eliminated.

[0047] FIG. 4 is a micrograph of a GaN surface grown under moderately high NH₃ partial pressure (moderate V:III ratio). This particular GaN film was grown on an AlN-coated sapphire substrate. The growth rate was about 320 microns per hour, the GaCl partial pressure was around 1.8 Torr, the NH₃ partial pressure was around 112.8 Torr, the V:III ratio was around 58, and the growth temperature was about 990° C. The growth time was 20 minutes. Although the GaN film surface is covered with pits, the film is still epitaxial single-crystalline film, as confirmed by x-ray rocking curve measurement, with FWHM of 400 arcsec. The larger FWHM value of the film is due in part to curvature of the sample, which is known to broaden the X-ray diffraction peak.

[0048] Similar surface morphology trends are observed with growth temperature at otherwise constant conditions, or with growth rate at otherwise constant conditions. Under constant GaCl and NH₃ partial pressures (constant growth rate and V:III ratio), reducing the growth temperature alters the growth morphology from a smooth, hillock structure to a pitted surface morphology and eventually to a polycrystalline morphology. Similarly, at a constant growth temperature and V:III ratio, increasing the growth rate (by increasing both GaCl and NH₃ partial pressure) alters the surface morphology from a smooth pit-free surface to a pitted surface morphology and eventually to a polycrystalline morphology.

[0049] The pitted surface morphology eliminates the microcracks in the GaN film during the HVPE GaN growth. However, the surface is not desirable as a foundation of further growth of GaN-based device structures. The present invention discloses methods for growing high-quality, low defect density, pit-free and crack-free GaN films by hydride vapor phase epitaxy. The GaN films are suitable for the further growth of electronic and optoelectronic devices based on group III nitride alloys.

[0050] The GaN growth method of the present invention may include several growth steps, including depositing an epitaxial nitride template layer on a suitable substrate, growing a thin GaN layer on the nitride-coated substrate under a condition that yields a surface covered with pits, and growing a GaN layer on or from the pitted GaN layer under a condition that fills the pits and yields a pit-free surface.

[0051] According to this implementation, the first step of the growth process is to deposit a thin epitaxial nitride (e.g., AlN) layer on a suitable substrate such as, for example, sapphire. The purpose of this epitaxial nitride layer is to provide a template for epitaxial growth of GaN. Without the epitaxial nitride template, the HVPE GaN film grown on a substrate such as sapphire under typical conditions is polycrystalline. The epitaxial nitride layer in one implementation is prepared by high-temperature reactive sputtering in a sputtering chamber. An aluminum target and an AC plasma of an inert gas or gas mixture (e.g., an Ar/N₂ gas mixture) may be utilized to deposit the epitaxial nitride layer on a heated substrate. The epitaxial nitride layer may alternatively be formed by molecular beam epitaxy (MBE), metal-organic vapor phase epitaxy (MOVPE or MOCVD), hydride vapor phase epitaxy, or high-temperature annealing in ammonia. In one example, the thickness of the epitaxial nitride layer is in the range (ranges) from about 0.05 to about 2 microns. In another example, the thickness of the epitaxial nitride layer ranges from about 0.2 to about 2 microns. Other types of template layers may alternatively be used, for example, GaN or AlGaIn layers, grown by MOVPE, MBE or HVPE.

[0052] The second step of the growth process is to grow a GaN layer by hydride vapor phase epitaxy in a growth condition that yields pitted surface morphology. The nitride-coated substrate is loaded into a HVPE reactor, and the reactor may be purged with high purity nitrogen to remove impurities. A layer of gallium nitride is then grown on the epitaxial nitride layer. The growth condition for this GaN layer is typically higher growth rate, and/or higher ammonia flow (or V:III ratio), and/or lower growth temperature than the "optimal" thin-film growth condition. The "optimal" thin film growth condition is one that would produce smooth, substantially pit-free, crack-free thin films (e.g., with a thickness equal to or less than 3 microns), but would produce microcracked thick films (e.g., with a thickness equal to or greater than 20 microns). As one specific example of an optimized growth condition, a 1-micron thick GaN film that is transparent and has a smooth specular surface has been grown on an AlN-coated sapphire substrate by the inventors. The growth rate was about 60 microns per hour, the GaCl partial pressure was about 3 Torr, the NH₃ partial pressure was about 45 Torr, the V:III ratio was about 15, the growth temperature was about 950° C., and the growth time was one minute. When growing a thin film ($\leq 3 \mu\text{m}$), this "optimal" thin-film growth condition typically

produces a crack-free film, whereas when growing a thick film (≥ 20 μm), the "optimal" growth condition typically produces a microcracked film.

[0053] The GaN film grown under the growth condition of this second step is very rough and covered with pits. There are two purposes for this pitted layer: first is to prevent microcracking of GaN during the growth; and second is to promote annihilation of dislocations. In one example, the thickness of this pitted layer ranges from approximately 2 to approximately 50 microns. In another example, the thickness of this pitted layer ranges from approximately 5 to approximately 50 microns. If the GaN film is grown under the pitted growth condition with higher thickness, the GaN film quality is gradually changed from an epitaxial single-crystalline film to a polycrystalline film.

[0054] In one implementation, the growth temperature during growth of the first (pitted) epitaxial GaN layer ranges from about 900° C. to about 1000° C., the V:III ratio ranges from about 10 to about 100, and the growth rate ranges from about 50 $\mu\text{m/hr}$ to about 500 $\mu\text{m/hr}$.

[0055] The third step of the growth process is to grow an additional GaN layer under conditions that cause the pits to be filled and yield a pit-free and crack-free surface. The growth condition for this layer is typically lower growth rate, and/or lower ammonia partial pressure, and/or higher growth temperature than the growth condition utilized for the pitted layer. The thickness of this layer is in one example greater than about 3 microns, in another example greater than about 5 microns, and in another example greater than about 10 microns. In another example, the thickness of second epitaxial GaN layer ranges from about 3 to about 200 microns. In another example, the thickness of second epitaxial GaN layer ranges from about 8 to about 200 microns. The optimal thickness of the pit-free layer depends on the thickness of the pitted layer. A thicker layer grown under pitted growth conditions correspondingly requires a thicker layer grown under pit-free conditions to completely fill the pits. The ratio of the thickness of the layer grown under pitted conditions to the thickness of the layer grown under pit-free condition is in one example between about 2:1 and about 1:5.

[0056] In one implementation, the growth temperature during growth of the second epitaxial GaN layer ranges from about 920° C. to about 1100° C., the V:III ratio ranges from about 8 to about 80, and the growth rate ranges from about 5 $\mu\text{m/hr}$ to about 500 $\mu\text{m/hr}$.

[0057] FIG. 5 is a schematic illustration of an exemplary growth process 500 of the present invention. First, a substrate 504 is provided. An epitaxial nitride (e.g., AlN) layer 508 is then deposited on the substrate 504. The deposition of the epitaxial nitride layer 508 may be done in the same reactor for the subsequent GaN growth or in a different deposition chamber. GaN material is subsequently deposited on the nitride-coated substrate 504/508 by hydride vapor phase epitaxy in two steps with different growth conditions. A first GaN layer 512 is grown under a condition that results in a pitted surface morphology, and such conditions are characterized by relatively higher growth rate, and/or high ammonia flow, and/or lower growth temperature than utilized during the second GaN growth step. A second GaN layer 516 is then grown under a condition that fills the pits on the surface 514 of the first GaN layer 512 and yields

pit-free smooth GaN layer, and such growth conditions are characterized by relatively lower growth rate, and/or lower ammonia flow, and/or higher growth temperature than employed in the first, pitted-growth step. The combination of the two GaN growth steps both eliminates the GaN microcracking during the growth and provides a smooth, low-defect GaN surface 518 that is suitable for the further growth of devices based on Group III nitrides. The growth process 500 yields a GaN film generally depicted at 524 in FIG. 5.

[0058] The substrate 504 may be any substrate that has a surface having a 3-fold symmetry or close to having a 3-fold symmetry. Some examples of the present disclosure utilize c-plane sapphire as the substrate 504. Other substrates 504 such as silicon, silicon carbide, diamond, lithium gallate, lithium aluminate, zinc oxide, spinel, magnesium oxide, and gallium arsenide may be utilized for the growth of low-defect, crack-free GaN films. In one example, the substrate 504 has a characteristic dimension (e.g., diameter) of about 2 inches or greater. In other examples, the diameter of the substrate 504 is about 2" or greater, about 3" or greater, about 4" or greater, or any other suitable size.

[0059] The substrate surface 506 may be exactly c-plane or vicinal surfaces of the c-plane. Vicinal surfaces may promote step-flow during the HVPE GaN growth and may yield smoother surface morphology. The offcut angle of the vicinal surface with respect to the c-plane in one example ranges from about 0° to about 10°, in another example from about 0.10 to about 100, and in another example from about 0.50 to about 5°. The direction of offcut may be along the <1-100> direction or along the <11-20> direction, or along a direction between <1-100> and <11-20>.

[0060] In some implementations, the deposition of the epitaxial nitride layer 508 may be needed to grow single-crystalline GaN films on substrates 504 such as sapphire substrates using the HVPE process. In one implementation, the epitaxial nitride layer 508 is deposited by reactive sputtering on a heated substrate 504 in a sputter deposition chamber. The nitride-coated substrate 504/508 is subsequently removed from the sputter chamber and loaded into the HVPE reactor for GaN growth. As alternatives to depositing AlN by HVPE, other nitride layers, such as AlN grown by MOCVD, GaN grown by MOCVD, AlGaIn grown by MOCVD, and the like may also be used. A reactive sputtering-deposited AlN layer has the advantage of lower cost than MOCVD or MBE deposited nitride layers. AlN layers may also be grown in the HVPE reactor by incorporating an Al source so that hydrochloric acid reacts with Al to form aluminum chloride that reacts with ammonia in the deposition zone to form AlN on the substrate surface 506.

[0061] The growth of GaN film 524 according to this implementation includes at least two growth steps with different growth conditions. The growth temperature is typically between 900° C. and 1100° C., the growth rate is typically between 5 and 500 microns per hour, and V:III ratio is typically between 5 and 100. The two-step GaN growth is characterized by the growth conditions of the first step having lower growth temperature, and/or higher ammonia flow, and/or higher growth rate than the second step. In one example, the growth temperature is about 15° C. hotter in the second step than in the first step, and the growth rate of the second step is about one-fourth of the first step. At the end

of the first step, the GaN surface **514** is rough and covered with the pits. If the growth is stopped at the end of the first step and wafer is taken out of the reactor, the GaN surface **514** is not specular, as shown in a microphotograph in FIG. 6. The pit coverage, defined as the percentage of a surface covered with the pits on the surface, is in one example greater than about 50%, and in another example greater than about 75%, and in another example greater than about 90% at the end of the first GaN growth step. At the end of the second step, the GaN surface **518** is smooth, specular and pit-free. The pit coverage in the final film is in one example less than 1%, in another example less than 0.1%, and in another example less than 0.01%.

[0062] The resulting GaN film **524** may have a characteristic dimension (e.g., diameter) as large as the initial substrate **504**. As examples, when a 2" substrate **504** is utilized, a 2" GaN film **524** may be obtained. When a 3" substrate **504** is utilized, a 3" GaN film **524** may be obtained. When a 4" substrate **504** is utilized, a 4" GaN film **524** may be obtained. The thicknesses of the respective GaN layers **512** and **516** grown in the two steps is in one example in a ratio between about 2:1 and about 1:5, and in another example in a ratio between about 1:1 and about 1:3, and in another example in a ratio between about 1:1 and about 1:2. The exact conditions of the two steps may strongly depend on the reactor configuration and method of temperature measurement, and may be easily found by those skilled in the arts. The total thickness of the GaN film **524** in one example ranges from approximately 10 to approximately 250 microns, in another example from approximately 10 to approximately 200 microns, and in another example from approximately 20 to approximately 100 microns, and in another example from approximately 20 to approximately 50 microns.

[0063] The HVPE GaN layers **512** and **516** may be grown without intentionally introduced impurities. However, because of the crystal defects and residual impurities such as oxygen and silicon from the reactor, an unintentionally doped GaN layer may still have n-type conductivity. The GaN may also be grown with the presence of intentionally introduced impurities such as silane or oxygen for n-type doping, or magnesium for p-type doping. When transition metal impurities are introduced, the GaN film **524** can be made semi-insulating. Transitional metal impurities, such as iron, may be introduced using, for example, volatile metal-organic compounds such as ferrocene. It will be understood that the growth conditions may be slightly different when the doping impurities are introduced. In one example, the dopant concentration (e.g., n-type, p-type, transition metal, etc.) is greater than about $1 \times 10^{18} \text{ cm}^{-2}$. In one example of a semi-insulating GaN film **524** produced according to the present disclosure, the GaN film **524** has a resistivity greater than about $1 \times 10^5 \text{ ohm-cm}$.

[0064] Because of the thermal mismatch between the substrate **504** and the GaN film **524**, the wafer is bowed after cool-down from the growth temperature to the ambient temperature. The bow of the wafer complicates the device fabrication process and a large bow of the wafer is not desirable. One aspect of the present invention is that the GaN material during growth develops a tensile stress that will compensate the thermal stress and reduce the wafer bow. The tensile stress of the GaN material during the growth is associated with the reduction of dislocations in the GaN material. In another implementation of the present

invention, a thicker substrate **504** may also be employed to reduce the GaN film bow. In another implementation, the backside of the substrate **504** is mechanically lapped to introduce damage on the backside of the substrate **504**, which reduces the bow of the GaN film **524** on the substrate **504**. In one example, the wafer bow is less than about 200 microns. In another example, the wafer bow is less than about 100 microns. In another example, the wafer bow is less than about 50 microns. In another example, the wafer bow is less than about 25 microns. Wafer bow may be defined as the deviation of the center point of the median surface of the wafer from a median-surface reference plane of the wafer.

[0065] As an example of wafer bowing, FIG. 7 illustrates a bowed wafer **704** having a bowed median surface **708** with a center point **712**. A median surface reference plane **716** with a center point **720** is established by three equally-spaced points on the median surface at the wafer circumference. In this example, the wafer bow *b*, projected to the right of the bowed wafer **704**, is the distance between the center point **712** in the median surface of a free unclamped wafer and the center point **720** in the median surface reference plane **716**. It will be understood that the radius of curvature of the bowed wafer **704** as depicted in FIG. 7 is exaggerated for illustrative purposes.

[0066] The crystal defect density, specifically, threading dislocation density, decreases with the thickness of the GaN film grown. In implementations described in the present disclosure, the lattice mismatch between the GaN material and substrate that generates dislocation is first accommodated by the AlN layer. The dislocations in the GaN material are further annihilated during the two-step GaN growth. The reduction of dislocation density during HVPE GaN growth according to implementations described in the present disclosure is much faster than those disclosed in the prior arts. For example, U.S. Pat. Nos. 6,533,874 and 6,156,581 disclose a GaN base structure grown by an HVPE process. According to the prior art, the dislocation density of a 10-micron thick GaN film grown by HVPE on sapphire is approximately 10^9 cm^{-2} , and the dislocation density is reduced to approximately 10^8 cm^{-2} for a 23-micron GaN film, and to approximately 10^7 cm^{-2} for a 300-micron GaN film. In implementations of the present invention, improved GaN films have been grown by HVPE on sapphire, as represented by the following examples: a dislocation density on the surface less than 10^8 cm^{-2} for a 10-micron GaN film, less than $5 \times 10^7 \text{ cm}^{-2}$ for a 20-micron GaN film, and less than $2 \times 10^7 \text{ cm}^{-2}$ for a 50-micron GaN film. The surface dislocation density of GaN film grown according to implementations of the present invention is approximately several factors lower than GaN films of the prior art at similar thickness. According to some examples of the invention, the threading dislocation density on the surface of the GaN film may be less than $1 \times 10^8 \text{ cm}^{-2}$, in other examples less than $5 \times 10^7 \text{ cm}^{-2}$, in other examples less than $1 \times 10^7 \text{ cm}^{-2}$, and in other examples less than $5 \times 10^6 \text{ cm}^{-2}$.

[0067] The wafer structure and method for making the structure of the present invention differ substantially from the prior art of U.S. Pat. Nos. 6,533,874 and 6,156,581. We were not able to grow device-quality epitaxial single-crystal GaN films using the methods taught by prior art such as in these patent references. By contrast, in accordance with the present invention, including the use of the epitaxial nitride

template layer **508** (FIG. 5) described above, we can reproducibly grow device-quality epitaxial single-crystal GaN films by HVPE. Additionally, the present invention discloses methods for eliminating GaN film microcracking during HVPE GaN growth. Microcracking of GaN film during the HVPE growth and methods for eliminating the growth microcracking have not been disclosed in the prior art. Implementations of the present invention employ a two-step HVPE GaN growth process to eliminate the growth microcracking and to produce smooth surfaces on the GaN films.

[0068] Low-defect single-crystal film of Group III nitride alloys, $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$ ($x+y+z=1$, $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$), may be similarly grown according to additional embodiments of the present invention. An AlN nucleation layer is first deposited on a substrate. Single-crystal $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$ film is grown on the AlN-coated substrate by HVPE using the two-step growth process described above. The $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$ film is grown under a condition that yields a pitted surface morphology in the first step and then under a growth condition that promotes filling the pits to produce a smooth surface morphology in the second step. Typically, the first step has a lower growth temperature, and/or higher growth rate, and/or higher ammonia flow than the second growth step. The exact condition for the two-step $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$ growth depends on the reactor configuration and film composition, and may be easily determined by those skilled in the art. Thus, as previously noted, the term "GaN" encompasses " $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$."

[0069] The surface morphology of the low-defect GaN film **524** may be further improved by using a chemical mechanical polish (CMP). The as-grown HVPE GaN film may exhibit some hillock features as shown in FIG. 8. In some applications, the macroscopic roughness of the GaN film surface **518** (FIG. 5) is less desirable for further device layer growth. The GaN film surface **518** may be improved by chemical mechanical polish. The CMP process does not produce surface and subsurface damage on the GaN film surface **518** because of the active chemical etching during the polish.

[0070] The present invention can be further understood by following illustrative, non-limiting examples.

EXAMPLE 1

Low-Defect GaN Film Growth

[0071] In this example, we illustrate the growth of a high-quality, low-defect GaN film suitable for the further growth of electronic and optoelectronic devices. A 2"-diameter, 430-micron thick sapphire was used as the starting substrate. Using the sputtering method disclosed in U.S. Pat. No. 6,784,085, an AlN layer approximately 0.7 μm thick was grown on the sapphire substrate for use as a template layer for the HVPE GaN growth. X-ray diffraction was used to verify the AlN film was single-crystal. The AlN/sapphire structure was loaded into a vertical HVPE system and the GaN growth was commenced.

[0072] The HVPE GaN film was grown by a two-step method. The GaN film was first grown under conditions of growth rate of approximately 260 microns per hour, growth temperature of 955° C., HCl flow rate of 92 sccm, and NH_3 flow rate of 2500 sccm. After growth of approximately 4 minutes under these growth conditions, the growth rate was

reduced to approximately 65 microns per hour by reducing HCl flow to 23 sccm, and growth temperature was raised by 20° C. After growth of approximately 7 minutes under these conditions, the NH_3 flow was further reduced to 750 sccm for approximately 32 minutes. The total grown GaN film thickness was approximately 60 microns. The bow of the wafer was approximately 190 microns. The GaN film was specular visually, and under optical microscope observation, hillock features were present on the surface as shown in FIG. 8.

[0073] An atomic force microscope (AFM) was used to image the wafer surface and to measure the threading dislocation density. A threading dislocation terminates on the surface as a pit that can be observed with AFM. FIG. 9 is a 10-micron by 10-micron AFM scan of the wafer surface. The pit density, i.e., the threading dislocation density on the surface, was approximately $1.9 \times 10^7 \text{ cm}^{-2}$.

EXAMPLE 2

Low-defect GaN Film Growth

[0074] In this example, we illustrate the growth of another high-quality, low-defect GaN film suitable for the further growth of electronic and optoelectronic devices. A 2"-diameter 430-micron thick sapphire was used as the starting substrate. Using the sputtering method disclosed in U.S. Pat. No. 6,784,085, an AlN layer approximately 0.7 μm thick was grown on the sapphire substrate for use as a template layer for the HVPE GaN growth. The AlN/sapphire structure was loaded into a vertical HVPE system and the GaN growth was commenced.

[0075] The HVPE GaN film was grown by a two-step method. The GaN film was first grown under conditions of growth rate of approximately 260 microns per hour, growth temperature of 955° C., HCl flow rate of 92 sccm, and NH_3 flow rate of 2500 sccm. After growth of approximately 3 minutes under these growth conditions, the growth rate was reduced to approximately 30 microns per hour by reducing the HCl flow rate to 10 sccm. At the same time, the growth temperature was raised by 20° C. and the NH_3 flow rate was reduced to 400 sccm for an additional 25 minutes. The total grown GaN film thickness was approximately 25 microns. The bow of the wafer was approximately 95 microns. The GaN film was specular visually, and under optical microscope observation hillock features were present on the surface.

EXAMPLE 3

Low-defect GaN Film Growth with Lapping Treatment

[0076] The GaN film on sapphire obtained from Example 2 is mounted on a stainless steel plate using wax with the GaN film facing the plate. The backside of the sapphire substrate is lapped on a metal lapping plate with 30-micron diamond slurry. After removing approximately 10 microns from the backside of the sapphire substrate, the wafer bow is reduced from approximately 95 microns to approximately 40 microns.

EXAMPLE 4

Low-Defect GaN Film Growth with Polishing Treatment

[0077] The GaN film on sapphire obtained from Example 3 is mounted on a stainless steel plate using wax with the

GaN film facing up. The surface of the GaN film is then chemical mechanically polished to remove approximately one micron of surface material. The root-mean square (RMS) surface roughness of the GaN film is reduced from approximately 5 nm for the as-grown film to approximately 0.5 nm or less for the CMP polished surface.

[0078] The examples of the present invention utilized several specific growth sequences. It should be understood that these specific growth process are meant for purposes of illustration and not to be limiting. It should also be noted that growth conditions cited in the examples are specific to the HVPE growth reactor used in the examples. Different reactor design or reactor geometry may need a different condition to achieve similar results. However, the general trends are still similar.

[0079] It will be apparent to those skilled in the art that various modifications and variations can be made in the growth of low defect density GaN film within the scope of the present invention. Thus it is construed that the present invention covers the variations and modifications of this invention provided they come within the scope of the appended claims and their equivalent.

What is claimed is:

1. A method for making a low-defect single-crystal gallium nitride (GaN) film, comprising:

depositing an epitaxial aluminum nitride (AlN) layer on a substrate;

growing a first epitaxial GaN layer on the AlN layer by HVPE under a growth condition that promotes the formation of pits, wherein after growing the first GaN layer the GaN film surface morphology is rough and pitted; and

growing a second epitaxial GaN layer on the first GaN layer to form a GaN film on the substrate, wherein the second GaN layer is grown by HVPE under a growth condition that promotes filling of the pits, and after growing the second GaN layer the GaN film surface morphology is essentially pit-free,

wherein the GaN growth condition for growing the first GaN layer is selected from the group consisting of a higher growth rate than during growth of the second GaN layer, a lower growth temperature than during growth of the second GaN layer, a higher ammonia flow than during growth of the second GaN layer, and two or more of the foregoing.

2. The method of claim 1, wherein the substrate is sapphire.

3. The method of claim 1, wherein the substrate is selected from the group consisting of sapphire, silicon, silicon carbide, diamond, lithium gallate, lithium aluminate, zinc oxide, spinel, magnesium oxide, and gallium arsenide.

4. The method of claim 1, wherein the substrate has surface orientation ranging from about 0° and about 5° with respect to a (0001) crystal orientation.

5. The method of claim 1, wherein the epitaxial AlN layer is deposited by high temperature reactive sputtering.

6. The method of claim 1, wherein the epitaxial AlN layer is deposited by a technique selected from a group consisting of sputtering, molecular beam epitaxy, metal-organic vapor phase epitaxy, hydride vapor phase epitaxy, and annealing in ammonia.

7. The method of claim 1, wherein the thickness of the deposited AlN layer is between approximately 0.05 and approximately 2 microns.

8. The method of claim 7, wherein the thickness of the grown first GaN layer ranges from approximately 2 to approximately 50 microns, and the thickness of the grown second GaN layer is approximately 3 microns or greater.

9. The method of claim 1, wherein the GaN surface morphology after growing the first GaN layer is not specular and has a pit coverage greater than 50%.

10. The method of claim 1, wherein the growth condition for the first GaN layer includes a first GaN layer growth temperature ranging from about 900° C. to about 1000° C., a first GaN layer V:III ratio ranging from about 10 to about 100, and a first GaN layer growth rate ranging from about 50 μm/hr to about 500 μm/hr.

11. The method of claim 10, wherein the growth condition for the second GaN layer includes a second GaN layer growth temperature ranging from about 920° C. to about 1100° C., a second GaN layer V:III ratio ranging from about 8 to about 80, and a second GaN layer growth rate ranging from about 5 μm/hr to about 50 μm/hr.

12. The method of claim 1, wherein the thickness of the grown first GaN layer ranges from approximately 2 to approximately 50 microns.

13. The method of claim 1, wherein the growth condition for the second GaN layer includes a growth temperature ranging from about 920° C. to about 1100° C., a V:III ratio ranging from about 8 to about 80, and a growth rate ranging from about 5 μm/hr to about 500 μm/hr.

14. The method of claim 1, wherein the thickness of the grown second GaN layer is about 3 microns or greater.

15. The method of claim 1, wherein the thickness of the grown second GaN layer ranges from approximately 3 to approximately 200 microns.

16. The method of claim 1, wherein the total thickness of the GaN film after growing the second GaN layer ranges from approximately 10 to approximately 250 microns.

17. The method of claim 1, wherein the ratio of the thickness of the grown first GaN layer to the thickness of the grown second GaN layer ranges from approximately 2:1 to approximately 1:5.

18. The method of claim 1, wherein the GaN film has a characteristic dimension of about 2 inches or greater.

19. The method of claim 1, wherein the threading dislocation density on the GaN film surface after growing the second GaN layer is less than $1 \times 10^8 \text{ cm}^{-2}$.

20. The method of claim 1, wherein the threading dislocation density on the GaN film surface after growing the second GaN layer is less than $5 \times 10^7 \text{ cm}^{-2}$.

21. The method of claim 1, wherein the threading dislocation density on the GaN film surface after growing the second GaN layer is less than $1 \times 10^7 \text{ cm}^{-2}$.

22. The method of claim 1, wherein the threading dislocation density on the GaN film surface after growing the second GaN layer is less than $5 \times 10^6 \text{ cm}^{-2}$.

23. The method of claim 1, further including polishing the GaN film.

24. The method of claim 23, wherein the surface root-mean square roughness of the GaN film after polishing is about 0.5 nm or less.

25. The method of claim 1, further including, after growing the second GaN layer, mechanically lapping a back side of the substrate.

26. The method of claim 1, wherein the bow of the GaN film on the substrate is less than 200 microns.

27. The method of claim 1, wherein the bow of the GaN film on the substrate is less than 100 microns.

28. The method of claim 1, wherein the bow of the GaN film on the substrate is less than 50 microns.

29. The method of claim 1, wherein the bow of the GaN film on the substrate is less than 25 microns.

30. A low-defect single-crystal GaN film produced according to the method of claim 1.

31. A low-defect single-crystal GaN film having a characteristic dimension of about 2 inches or greater, and a thickness normal to the characteristic dimension ranging from approximately 10 to approximately 250 microns, the GaN film including a pit-free surface, the threading dislocation density on the GaN film surface being less than $1 \times 10^8 \text{ cm}^{-2}$.

32. A low-defect single-crystal gallium nitride (GaN) on substrate structure, comprising:

a substrate;

an epitaxial aluminum nitride (AlN) layer on the substrate; and

a GaN film on the substrate, the GaN film including a first epitaxial GaN growth layer and a second epitaxial GaN growth layer, wherein:

the first epitaxial GaN layer is grown on the AlN layer under a growth condition that promotes the formation of pits, and after growing the first GaN layer the GaN film surface morphology is rough and pitted; and

the second epitaxial GaN is grown on the first GaN layer by HVPE under a growth condition that promotes filling of the pits formed, and after growing

the second GaN layer the GaN film surface morphology is essentially pit-free.

33. The GaN on substrate structure of claim 32, wherein the substrate is sapphire.

34. The GaN on substrate structure of claim 32, wherein the substrate is selected from the group consisting of sapphire, silicon, silicon carbide, diamond, lithium gallate, lithium aluminate, zinc oxide, spinel, magnesium oxide, and gallium arsenide.

35. The GaN on substrate structure of claim 32, wherein the thickness of the deposited AlN layer is between approximately 0.05 and approximately 2 microns, the thickness of the grown first GaN layer ranges from approximately 2 to approximately 50 microns, and the thickness of the grown second GaN layer is approximately 3 microns or greater.

36. The GaN on substrate structure of claim 32, wherein the total thickness of the GaN film ranges from approximately 10 to approximately 250 microns.

37. The GaN on substrate structure of claim 32, wherein the ratio of the thickness of the grown first GaN layer to the thickness of the grown second GaN layer ranges from approximately 2:1 to approximately 1:5.

38. The GaN on substrate structure of claim 32, wherein the GaN film has a characteristic dimension of about 2 inches or greater.

39. The GaN on substrate structure of claim 32, wherein the threading dislocation density on the GaN film surface is less than $1 \times 10^8 \text{ cm}^{-2}$.

40. The GaN on substrate structure of claim 32, wherein the surface root-mean square roughness is less than 0.5 nm.

41. The GaN on substrate structure of claim 32, wherein the bow of the GaN film on the substrate is less than 200 microns.

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