(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 September 2009 (03.09.2009)

PCT

(10) International Publication Number
WO 2009/108700 A1

(51) International Patent Classification:
C30B 33/02 (2006.01) ***C30B 29/40*** (2006.01)

(21) International Application Number:
PCT/US2009/035140

(22) International Filing Date:
25 February 2009 (25.02.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/067,117 25 February 2008 (25.02.2008) US

(71) Applicant *(for all designated States except US)*: **SIX-POINT MATERIALS, INC.** [US/US]; 37 Industrial Way, Unit 106, Buellton, CA 93427 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HASHIMOTO, Tadao** [JP/US]; 5066 Calle Real, B, Santa Barbara, CA 93111 (US). **LETTS, Edward** [US/US]; 371 Sycamore Drive, Buellton, CA 93427 (US). **IKARI, Masanori** [JP/US]; 3765 Lincoln Road, Santa Barbara, CA 93110 (US).

(74) Agent: **HOLLAND, Charles, D.**; Morrison & Foerster LLP, 755 Page Mill Road, Palo Alto, CA 94304-1018 (US).

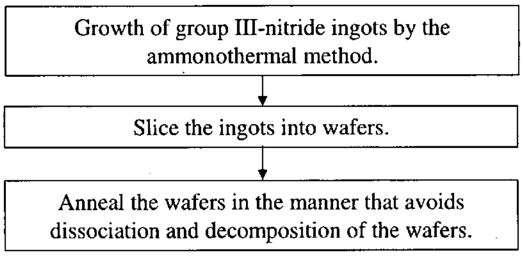
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: METHOD FOR PRODUCING GROUP III NITRIDE WAFERS AND GROUP III NITRIDE WAFERS

FIG. 1



(57) Abstract: The present invention discloses a production method for group III nitride ingots or pieces such as wafers. To solve the coloration problem in the wafers grown by the ammonothermal method, the present invention composed of the following steps; growth of group III nitride ingots by the ammonothermal method, slicing of the ingots into wafers, annealing of the wafers in a manner that avoids dissociation or decomposition of the wafers. This annealing process is effective to improve transparency of the wafers and/or otherwise remove contaminants from wafers.

WO 2009/108700 A1

METHOD FOR PRODUCING GROUP III NITRIDE WAFERS
AND
GROUP III NITRIDE WAFERS

BACKGROUND

[0001] This application claims the benefit of priority to U.S. App. Ser. No. 61/067,117 entitled "Method for Producing Group III Nitride Wafers and Group III Nitride Wafers," inventors Tadao Hashimoto, Edward Letts, and Masanori Ikari, filed Feb. 25, 2008, the contents of which are incorporated by reference herein in their entirety as if put forth in full below.

1. Field of the invention.

[0002] The invention is related to the production of group III nitride wafers using the ammonothermal method.

2. Further information on Group III-nitride materials and manner of making.

[0003] (Note: This patent application refers several publications and patents as indicated with numbers within brackets, e.g., [x]. A list of these publications and patents can be found in the section entitled "References.")

[0004] Gallium nitride (GaN) and its related group III alloys are the key material for various opto-electronic and electronic devices such as light emitting diodes (LEDs), laser diodes (LDs), microwave power transistors, and solar-blind photo detectors. Currently LEDs are widely used in cell phones, indicators, displays, and LDs are used in data storage discs. However, a majority of these devices are grown epitaxially on heterogeneous substrates, such as sapphire and silicon carbide, since GaN wafers are extremely expensive compared to these heteroepitaxial substrates. The heteroepitaxial growth of group III nitride causes highly defected or even cracked films, which hinders the realization of high-end optical and electronic devices, such as high-brightness LEDs for general lighting or high-power microwave transistors.

[0005] To solve fundamental problems caused by heteroepitaxy, it is useful to utilize single crystalline group III nitride wafers sliced from bulk group III nitride crystal ingots. For a majority of devices, single crystalline GaN wafers are favorable because it is relatively easy to control the conductivity of the wafer, and GaN wafer will provide smallest lattice/thermal mismatch with device layers. However, due to high melting point and high nitrogen vapor pressure at high temperature, it has been difficult to grow group III nitride crystal ingots. Growth methods using molten Ga, such as high-pressure high-temperature synthesis [1,2] and sodium flux [3,4], have been proposed to grow GaN crystals, nevertheless the crystal shape grown in molten Ga favors thin platelet formation because molten Ga has low solubility of nitrogen and a low diffusion coefficient of nitrogen.

[0006] An ammonothermal method, which is a solution growth method using high-pressure ammonia as a solvent, has demonstrated successful growth of bulk GaN ingots [5]. This newer technique called ammonothermal growth has a potential for growing large GaN crystal ingots, because high-pressure ammonia used as a fluid medium has high solubility of source materials, such as GaN polycrystals or metallic Ga, and has high transport speed of dissolved precursors.

[0007] However, state-of-the-art ammonothermal method [6-8] can only produce brownish crystals. This coloration is mainly attributed to impurities. In particular, oxygen, carbon and alkali metal concentration of the sliced wafers from GaN ingots is extremely high. The brownish wafer shows large optical absorption, which deteriorates the efficiency of light emitting devices grown on such wafers.

SUMMARY OF THE INVENTION

[0008] The present invention provides a new production method for group III nitride wafers. In one embodiment of the invention, after group III nitride ingots are grown by the ammonothermal method, the ingots are sliced into pieces such as wafers having a thickness between about 0.1 mm and about 1 mm, for instance. Then, the pieces are annealed in a manner that improves transparency of the pieces and avoids dissociation and/or decomposition of the pieces. A surface portion of the pieces may then be removed if desired.

[0009] Resultant pieces such as wafers may differ from other ingot-derived or individually-grown pieces or wafers in their (1) transparency and (2) in their amount and/or distribution of impurities or their surface morphology resulting from having a surface layer removed, or both.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

[0011] FIG. 1 is a flow chart for the production of group III nitride wafers;

[0012] FIG. 2 is an example of the ammonothermal growth apparatus. 1 reaction vessel, 2 lid, 3 gasket, 4 heater for the dissolution region, 5 heater for the crystallization region, 6 convection-restricting device, 7 group III-containing nutrient, 8 nutrient basket, 9 group III nitride seed crystals;

[0013] FIG. 3 is the concentration of heavy metal impurities before and after the annealing in Example 1 measured by secondary ion mass spectroscopy (SIMS). The unit of the concentration is atoms/cm3.

[0014] FIG. 4 is the concentration of light metal impurities before and after the annealing in Example 1 measured by secondary ion mass spectroscopy (SIMS). The unit of the concentration is atoms/cm^3.

DETAILED DESCRIPTION OF THE INVENTION

[0015] In the following description of the preferred embodiment, reference is made to 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.

Technical description of aspects of the invention

[0016] The present invention provides a method of producing group III (group 13) nitride wafers, primarily group III nitride single crystalline wafers that include at least one of the group III elements B, Al, Ga and In, such as GaN, AlN and InN. The process flow for one embodiment of the invention is indicated in FIG. 1. A group III nitride ingot is grown by the ammonothermal method, the ingot is cut into pieces, and the pieces are annealed preferably in a manner which limits or avoids dissociation and decomposition of piece surfaces. The pieces may be wafers as are typically used to form various semiconductor or optoelectronic devices, such as LEDs, laser diodes, solar cells, and photodetectors.

Ammonothermal growth of group III-nitride ingot

[0017] Ammonothermal ingot growth utilizes high-pressure NH_3 as a fluid medium, a nutrient containing at least one of the group III elements, and one or more seed crystals that are group III nitride single crystals. The high-pressure NH_3 provides high solubility of the nutrient and high transport speed of dissolved precursors. FIG. 2 shows an example of one ammonothermal reaction vessel in which the method may be carried out.

[0018] Methods of ammonothermal growth are discussed in WO08/51589 and in U.S. Application Serial Number 11/977,661, the contents of which are incorporated by reference in their entirety herein as if put forth in full below. The growth medium may therefore optionally contain a mineralizer. Basic mineralizers include Li, Na, K, $LiNH_2$, $NaNH_2$, and/or KNH_2. Acidic mineralizers include NH_4F, NH_4Cl, NH_4Br, and/or NH_4I.

[0019] Other ammonothermal growth methods may be used, such as those discussed in WO07/08198 and WO07/117689, which are incorporated by reference in their entirety herein as if put forth in full below.

[0020] The group III-nitride ingot (such as GaN) may be in the wurtzite crystal configuration or in the zincblende crystal configuration, for example.

Ingot slicing

[0021] After a group III nitride ingot is grown, the ingot is sliced into wafers or crystalline pieces of other shape(s). An ingot may be sliced by any suitable equipment or method. A cutter such as a mechanical saw (e.g. a wire saw), a dicing saw, or a laser may be used. Wafers cut from the ingot may have a thickness between about 0.1 mm and about 1 mm, for instance. Wafers or other ingot pieces may be cut from an ingot along a Group III element face of the crystal (e.g. Ga face of the crystal, (0001) face, (000-1) face, {11-20} face, {10-10} face or other low index planes.

Annealing wafer or other piece

[0022] Wafers or other ingot pieces are annealed to improve transparency and reduce impurities, preferably in a manner that limits or avoids substantial dissociation or decomposition of the pieces. Once pieces are cut from an ingot, those pieces may be individually or collectively annealed in an annealing reactor.

[0023] An annealing reactor may be configured to expose all surfaces of the piece (e.g. wafer) to an annealing gas in an annealing environment if desired. The annealing gas may be ammonia, hydrogen, a mixture of hydrogen and ammonia, or other gas that may create a reducing environment. While not being bound by theory, it is postulated that a reducing gas either maintains the pieces intact, without substantial degradation or decomposition or reacts with contaminants in the crystalline pieces, making the contaminants volatile and thereby removing the contaminants from the pieces, or both. The annealing gas may alternatively be an inert gas such as nitrogen, or the annealing gas may be a mixture of nitrogen, ammonia, and/or hydrogen and/or other gas that may create a reducing environment.

[0024] The annealing temperature may be selected to remove the amount of contaminant desired for removal. The temperature is sufficiently high to cause contaminants to migrate within the piece or pieces being annealed. For GaN, the temperature is often between about 500 and 1300°C. Typically, the temperature is at or above 500, 700, 800, 900, 1000, 1100, or 1200°C in ambient gas comprising NH_3 and H_2. At about 1300°C, the pieces being annealed may decompose or etch somewhat. Consequently, it may be desirable to anneal at a temperature of no more than about 1300°C in NH_3 and H_2 ambient. An annealing temperature of 1200°C works well.

[0025] The pieces are annealed for a sufficient length of time to remove contaminants to a desired concentration in the pieces. Pieces may be annealed for at least about 15, 30, 45, or 60 minutes, for instance. If a lower temperature is used, often pieces may be annealed for a longer period of time to reduce contaminant concentration to the desired level. Although the annealing time depends on annealing temperature, the length of time that the pieces or ingot are annealed is sufficiently long to remove contaminants but not too long in order to avoid substantial degradation of crystal quality.

[0026] It has been observed that certain contaminants such as alkali metals concentrate at a Ga face of the crystal. Likewise, alkaline earth metals may concentrate at a Ga face. The annealing gas may be preferentially directed at the Ga face in order to reduce the concentration of these contaminants in the crystalline pieces or ingot. The length of time and annealing temperature may be selected based on the high concentration of these contaminants at a Ga face, and therefore the annealing conditions such as temperature and time may be different than for the case where these contaminants are dispersed throughout the crystalline pieces.

[0027] Annealing is typically carried out at atmospheric pressure (i.e. 1 bar). If the annealing temperature is close to the dissociation temperature, annealing can be carried out under pressure, for instance at or above 10 bar, 100 bar, or 1000 bar. On the other hand, if major contaminants are less volatile material, annealing can be carried out at subatmospheric or low pressure, for instance at or below 100 mbar, 10 mbar, 1 mbar, or less.

Ingot annealing

[0028] A similar method can be utilized on the ingot itself. The ingot may be annealed in an annealing environment that limits or avoids substantial ingot dissociation or decomposition. The ingot may be annealed in addition to annealing pieces such as wafers cut from the ingot, or the ingot may be annealed instead of annealing its pieces.

Optional surface removal

[0029] Impurities may be further reduced by removing a surface layer of the wafers to which impurities have migrated. In one instance, at least a portion of a Group III element surface layer is removed (e.g. a Ga surface layer). Subsequent to ingot annealing, an outer surface or layer of the ingot may optionally be removed to reduce the concentration of the impurities in the ingot.

[0030] In some instances, any of the methods as discussed above reduce the concentration of heavy metals such as Ti, Cr, Fe, Ni, and Co (each metal alone or any combination of these heavy metals).

[0031] In some instances, any of the methods as discussed above reduce the concentration of alkali or alkaline earth metals such as Li, Na, Mg, and K (each metal alone or any combination of these metals). A portion of a surface layer may be removed that contains these metals, especially a Ga surface layer of the crystal of the ingot or wafer. The amount of surface of wafers or ingot that may be removed can vary depending upon how much impurity can be tolerated in the wafer or ingot during use.

Further considerations

[0032] The amount of impurity may be reduced by any method above to no more than about 60%, 50%, 40%, 30%, 20%, 15%, 10%, or 5% of the concentration of that impurity at a face (e.g. Ga or other group III element or nitride face) prior to annealing. Annealing may reduce the level of the contaminant to below a detectable level. See in particular the tables in Fig. 3 and 4, which indicate how much the concentration was reduced for various contaminants at the Group III element face and the nitride face. The concentration of contaminants was measured with secondary ion mass spectroscopy (SIMS).

[0033] The contaminant removed may be a metal. Alkali and alkaline earth metals may be removed in certain embodiments. Likewise, heavy metals selected from transition metals (e.g. Ti, Cr, Fe, Ni, and Co), metalloids such as Ge or heavier, rare earth metals, and other metals having similar atomic weight may be removed. The concentration of heavy metal impurities such as Ti, Cr, Fe, Ni or Co may be less than about 1×10^{17} cm^{-3} after an ingot or pieces are treated according to a method herein. The concentration of light metals (metals such as Li, Na, K, and Mg) may likewise be less than about 1×10^{17} cm^{-3} after an ingot or pieces are treated according to a method herein.

[0034] The annealing above differs from annealing after e.g. implanting a crystalline material with a dopant. Typically a substrate is annealed after implanting dopant atoms in order to diffuse the atoms to a certain depth and therefore decrease the concentration of the dopant in the substrate at the point of implantation. In the method of the invention, impurities may be concentrated locally (such as at a group III element face of the crystalline structure) rather than diffused, and/or impurities may be removed from the substrate by annealing it.

[0035] The annealed pieces or ingot may be used to form various electronic or optoelectronic devices. Electronic and optoelectronic devices include those disclosed in U.S. Application Serial Number 11/765,629, filed June 20, 2007 and entitled "Opto-Electronic and Electronic Devices Using N-Face or M-Plane GaN Substrate Prepared With Ammonothermal Growth", the contents of which are incorporated by reference herein in their entirety as if put forth in full below.

[0036] The following examples describe a detailed procedure within the scope of the current invention to help illustrate the invention further.

Example 1

[0037] In this example, a reaction vessel having an inner diameter of 1 inch was used for the ammonothermal growth. All necessary sources and internal components including 10 g of polycrystalline GaN nutrient held in Ni mesh basket, 0.3 mm-thick single crystalline GaN seeds, and three baffles, which acts as a flow restriction device were loaded into a glove box together with the reaction vessel. The glove box is filled with nitrogen and the oxygen and moisture concentration is maintained to be less than 1 ppm. Since the mineralizers are reactive with oxygen and moisture, the mineralizers are stored in the glove box all the time. 4 g of as-received $NaNH_2$ was used as a mineralizer. After loading mineralizer into the reaction vessel, three baffles together with seeds and nutrient are loaded. After closing the lid of the reaction vessel, it was taken out of the glove box. Then, the reaction vessel is connected to a gas/vacuum system, which can pump down the vessel as well as can supply NH_3 to the vessel. First, the reaction vessel was evacuated with a turbo molecular pump to achieve pressure less than 1×10^{-5} mbar. The actual pressure in this example was 1.2×10^{-6} mbar. In this way, residual oxygen and moisture on the inner wall of the reaction vessel are partially removed. After this, the reaction vessel was chilled with liquid nitrogen and NH_3 was condensed in the reaction vessel. About 40 g of NH_3 was charged in the reaction vessel. After closing the high-pressure valve of the reaction vessel, it was transferred to a two zone furnace. The reaction vessel was heated to 575 °C of the crystallization zone and 510 °C for the dissolution zone. After 7 days, ammonia was released and the reaction vessel was opened. The total thickness of the grown GaN ingot was 0.99 mm.

[0038] Since the thickness of the ingot was less than 1 mm, the ingot shape was already wafer-like without slicing. The wafer-like ingot had Ga-polar (0001) surface and N-polar (000-1) surface as basal planes. The wafer-shaped ingot was then loaded into an annealing reactor. The wafer-shaped ingot stood on its edge so that the both sides of the basal planes were exposed to the gas stream. After evacuating the air in the reactor, forming gas (4% H_2/96% N_2) was introduced to the reactor. Then, the reactor was heated. At 485 °C, ammonia was introduced to the reactor to suppress dissociation or decomposition. The flow rate of ammonia and the forming gas was 1 slm and 1.1 slm, respectively. The wafer-shaped ingot was annealed at 1100 °C for about 1 hour. Then, the reactor was cooled. At about 400 °C, ammonia was shut off.

[0039] The coloration in a wafer-like ingot prepared as described above was observably reduced when its coloration was compared to the coloration of a wafer-like ingot that was not annealed. This reduction in coloration in the annealed ingot indicates the reduction of impurities. The impurity quantification by secondary ion mass spectroscopy (SIMS) confirmed reduction of heavy metals such as Ti, Cr, Fe, Ni, and Co as shown in FIG. 3. On the other hand, light metals such as alkali metals and alkali earth metals moved toward Ga-polar surface. As shown in FIG. 4, the concentration of Li, Na, Mg, and K increased after annealing on the Ga-polar side whereas it decreased on the N-polar side. This suggests that alkali metals and alkali earth metals are positively charged and they are attracted by the surface charge on the Ga-polar surface, resulting in accumulation of these impurities on the top Ga-polar surface. Therefore, we can efficiently remove alkali metals and alkali earth metals from the wafer with annealing followed by removing a portion of the Ga-polar surface by e.g. grinding, lapping, polishing, or etching the Ga-polar surface.

Example 2

[0040] In this example a GaN ingot was formed by the same method as described in Example 1. The GaN ingot was sliced into 0.4 mm-thick wafers with a wire saw. Then 6 wafers were annealed at different temperatures (500, 700, 900, 1100, 1200, and 1300°C in NH_3 ambient for 1 hour) by the following process.

[0041] A wafer was placed into a reactor. After evacuating air in the reactor, a forming gas (4% H_2/96% N_2) was introduced into the reactor, and subsequently the reactor was heated. At 485°C, ammonia was introduced to the reactor to suppress dissociation or decomposition of the GaN. The flow rate of ammonia and the forming gas was 1 slm and 1.1 slm, respectively. During annealing both the Ga-face and the N-face of each wafer was exposed to the ambient gas. When the GaN wafer was annealed at 1300°C, the surface of the wafer was etched away. Therefore, if ammonia is used to suppress dissociation or decomposition, the temperature is typically less than 1300°C to avoid surface etching during annealing.

[0042] Properties of wafers annealed by the method above were compared to an unannealed wafer. Each wafer has three regions: a Ga-face region; a seed region; and a N-face region from the left in each wafer. The unannealed wafer had a dark N-face region and a slightly tinted Ga-face region together with a clear seed region. The coloration on the Ga-face was reduced with annealing even at 500°C. Slight reduction of coloration was observed for wafers annealed at 500, 700, 900, and 1100°C. Annealing at 1200°C made a drastic change: the N-face region showed much brighter color although the seed region and the Ga-face region showed slight coloration. Therefore, annealing at 1200 °C is effective for N-face region.

[0043] The following theory is of course not limiting on the scope of the invention. The difference in the coloration in the seed region and the Ga-face region implies that coloration is not only governed by an impurity, but also by native defects such as point defects. From the color change in the N-face region, it is believed that some impurities diffused out from the N-face region, thus the N-face region acted as an impurity source. The seed region, which was closer to the N-face region must have higher impurity concentration than Ga-face region which is farther from the N-face region. Therefore, if coloration is only due to impurity concentration, one might expect the seed region to be darker than the Ga-face region. However, the seed region was brighter than the Ga-face region. This implies that the Ga-face region originally had higher defects which, when combined with an impurity, will act as a color center. Therefore, it appears to be desirable to reduce native defects such as point defects in the ammonothermally grown group III-nitride crystals.

[0044] From this example, we found that annealing in ammonia is preferably performed at a temperature less than 1300 °C when surface etching of GaN is not desired, preferably between 500 and 1300 °C, or more preferably between 1100 and 1300 °C. The pressure may be about 1 bar, or the pressure may be sub-atmospheric or above atmospheric pressure as discussed above.

Advantages and Improvements

[0045] The present invention provides a new production method for group III nitride wafers with improved transparency and purity. Annealing the wafers after slicing is an effective way to reduce impurities in the crystal since the necessary time for the impurities to diffuse out of the crystal can be much smaller than the situation of annealing the ingot before slicing. The purified wafer showed improved transparency which improves efficiencies of optical devices fabricated on the wafers.

References

[0046] The following references are incorporated by reference herein as if put forth in full below:

[1]. S. Porowski, MRS Internet Journal of Nitride Semiconductor, Res. 4S1, (1999) G1.3.

[2] T. Inoue, Y. Seki, O. Oda, S. Kurai, Y. Yamada, and T. Taguchi, Phys. Stat. Sol. (b), 223 (2001) p. 15.

[3] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, and F. J. DiSalvo, J. Cryst. Growth 242 (2002) p.70.

[4] T. Iwahashi, F. Kawamura, M. Morishita, Y. Kai, M. Yoshimura, Y. Mori, and T. Sasaki, J. Cryst Growth 253 (2003) p. 1.

[5] T. Hashimoto, F. Wu, J. S. Speck, S. Nakamura, Jpn. J. Appl. Phys. 46 (2007) L889.

[6] R. Dwiliński, R. Doradziński, J. Garczyński, L. Sierzputowski, Y. Kanbara, U.S. Patent No. 6,656,615.

[7] K. Fujito, T. Hashimoto, S. Nakamura, International Patent Application No. PCT/US2005/024239, WO07008198.

[8] T. Hashimoto, M. Saito, S. Nakamura, International Patent Application No. PCT/US2007/008743, WO07117689. See also US20070234946, U.S. Application Serial Number 11/784,339 filed April 6, 2007.

[0047] Each of the references above is incorporated by reference in its entirety as if put forth in full herein, and particularly with respect to description of methods of making using ammonothermal methods and using these gallium nitride substrates.

Conclusion

[0048] This concludes the description of the preferred embodiment of the invention. The following describes some alternative embodiments for accomplishing the present invention.

[0049] Although the preferred embodiment describes the growth of GaN as an example, other group III nitride crystals may be used in the present invention. The group III nitride materials may include at least one of the group III elements B, Al, Ga, and In.

[0050] Although the preferred embodiment describes the annealing of ingots or wafers in ammonia ambient, other method to avoid dissociation or decomposition can be used. For example, covering the wafer surface with a silicon oxide layer, a silicon nitride layer, a metal layer or other protective layer is expected to be effective way to avoid dissociation and decomposition of the wafer. One or more of these layers may be deposited on a wafer using e.g. chemical vapor deposition or sputtering. If desired, the protective layer or layers may be removed using conventional etching techniques immediately before using a wafer to form a device.

[0051] Although the preferred embodiment describes the annealing at 1100 – 1200°C for 1 hour or other time sufficient to improve wafer clarity, other temperatures and/or times can be utilized so long as the same or similar benefit can be obtained.

[0052] In the preferred embodiment specific growth apparatuses and annealing apparatus are presented. However, other constructions or designs that fulfill the conditions described herein will have the same benefit as these examples.

[0053] The present invention does not have any limitations on the size of the wafer, so long as the same benefits can be obtained.

[0054] The foregoing description of the preferred embodiment 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.

WHAT IS CLAIMED IS:

1. A method for producing group III nitride crystalline pieces, comprising:
   (a) growing a group III nitride ingot by the ammonothermal method;
   (b) slicing a piece out of the ingot; and
   (c) annealing the piece for a time at a temperature and pressure sufficient to reduce a contaminant in said wafer.
2. The method of claim 1, wherein an annealing is carried out in a reducing ambient.
3. The method of claim 1 or claim 2, wherein the method further comprises concentrating a contaminant at a surface of the piece and removing an amount of the surface of the piece subsequent to step (c) to reduce the amount of the contaminant in the piece.
4. The method of any of claims 1-3, wherein an annealing temperature is at least about 500°C.
5. The method of any of claims 1-3, wherein the annealing temperature is at least about 800°C.
6. The method of any claim above, wherein the annealing temperature is no more than about 1300°C.
7. The method of claim 6, wherein the annealing temperature is between about 1100 and 1300°C.
8. The method of any claim above, wherein the reducing ambient comprises ammonia.
9. The method of any claim above, wherein the reducing ambient comprises hydrogen.
10. The method of any claim above, wherein step (c) is carried out after step (b).
11. The method of any claim above, wherein the piece is a wafer.
12. The method of claim 11, wherein the wafer thickness is between 0.1 mm and 1 mm.
13. The method of claim 11 or claim 12, wherein both sides of the wafer are exposed to the ambient.
14. The method of any claim above, wherein the group III nitride is GaN.

15. The method of claim 14, further comprising removing a portion of the Ga-polar side of the piece.

16. The method of claim 15, wherein the step of removing the portion of the Ga-polar side of the piece is carried out after step (c) of claim 1.

17. A group III nitride piece produced by any of the methods of claims 1-16.

18. A GaN piece produced by any of the methods of claims 1-16.

19. The GaN piece of claim 18, wherein the transparency of the piece is improved.

20. The GaN piece of claim 18, wherein the concentration of heavy metal impurities such as Ti, Cr, Fe, Ni or Co is less than about 1×10^{17} cm^{-3}.

21. The GaN piece of claim 18, wherein the concentration of light metal impurities such as Li, Na, K or Mg is less than about 1×10^{17} cm^{-3}.

22. A semiconductor device formed on a group III nitride piece of any of claims 17-21.

23. An optoelectronic device formed on a group III nitride piece of any of claims 17-21.

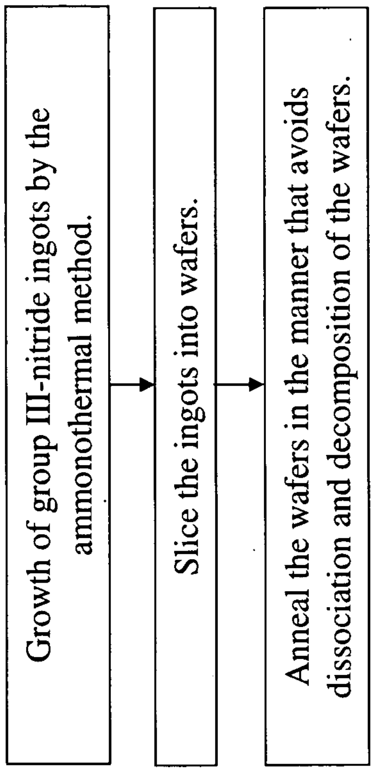

Growth of group III-nitride ingots by the ammonothermal method.
Slice the ingots into wafers.
Anneal the wafers in the manner that avoids dissociation and decomposition of the wafers.

FIG. 1

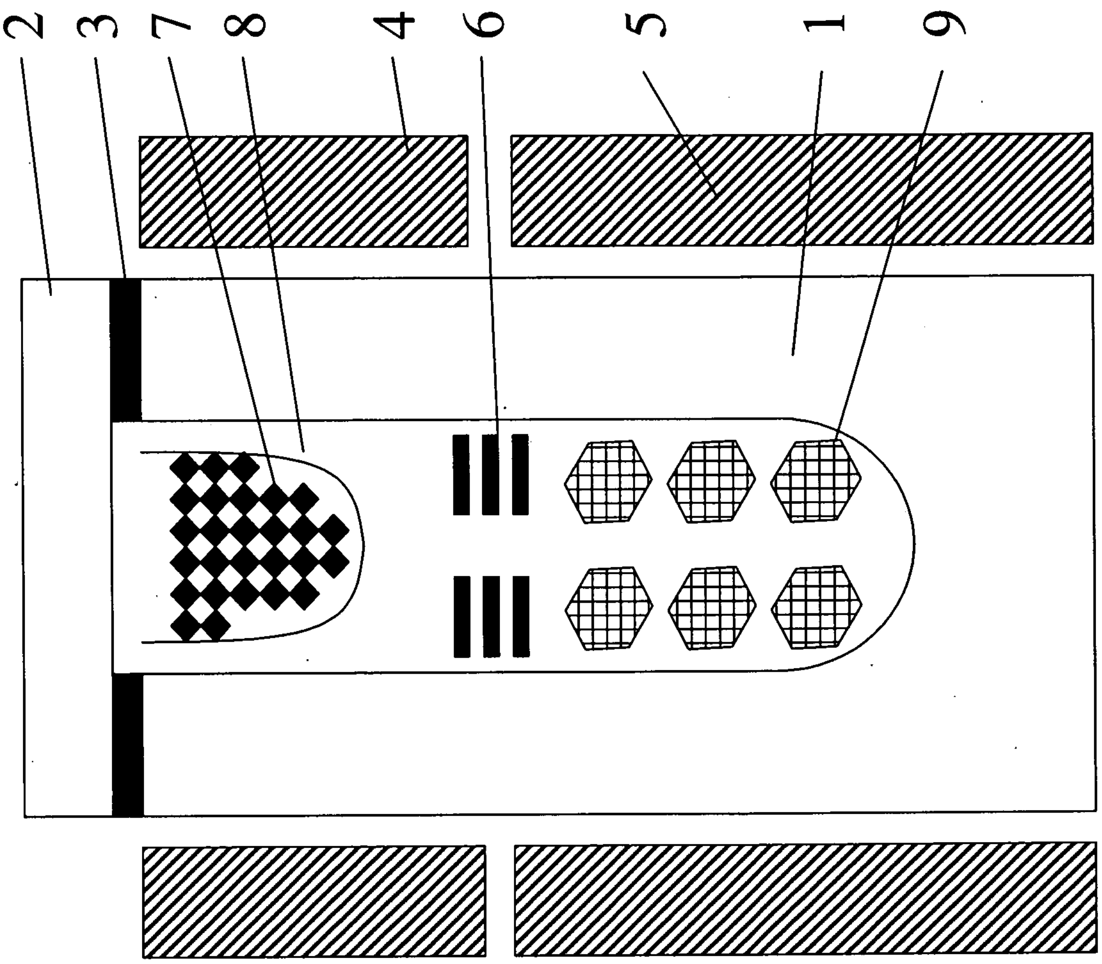


FIG. 2

FIG. 3

Sample ID	*Ti*	*Cr*	*Fe*	*Ni*	*Co*
1 Before anneal Ga -face	$7.0x10^{17}$	$1.3x10^{17}$	$2.3x10^{18}$	$2.2x10^{17}$	$1.0x10^{17}$
2 Before anneal N -face	$3.1x10^{17}$	$2.6x10^{16}$	$7.8x10^{17}$	$1.4x10^{17}$	$3.4x10^{16}$
3 After anneal Ga -face	$5.0x10^{16}$	$1.1x10^{16}$	$1.4x10^{18}$	$2.0x10^{16}$	$1.1x10^{16}$
4 After anneal -N-face	$1.2x10^{17}$	$\leq 6x10^{14}$	$3.0x10^{16}$	$1.0x10^{16}$	$9.0x10^{15}$
Detection Limit	**$8x10^{15}$**	**$6x10^{14}$**	**$9x10^{15}$**	**$8x10^{15}$**	**$2x10^{15}$**

FIG. 4

Sample ID	*Li*	*Na*	*Mg*	*K*
1 Before anneal Ga -face	$8.0\text{x}10^{14}$	$7.8\text{x}10^{18}$	$1.0\text{x}10^{17}$	$1.7\text{x}10^{16}$
2 Before anneal N -face	$2.0\text{x}10^{14}$	$1.2\text{x}10^{19}$	$1.2\text{x}10^{17}$	$4.0\text{x}10^{16}$
3 After anneal Ga -face	$1.2\text{x}10^{15}$	$2.4\text{x}10^{19}$	$1.2\text{x}10^{17}$	$4.1\text{x}10^{16}$
4 After anneal N -face	$4.0\text{x}10^{13}$	$2.0\text{x}10^{17}$	$3.9\text{x}10^{16}$	$<3\text{x}10^{14}$
Detection Limit	**$3\text{x}10^{13}$**	**$6\text{x}10^{14}$**	**$5\text{x}10^{14}$**	**$3\text{x}10^{14}$**

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/035140

A. CLASSIFICATION OF SUBJECT MATTER
INV. C30B33/02 C30B29/40

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)
C30B

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

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

EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/061923 A (GEN ELECTRIC [US]; D EVELYN MARK PHILLIP [US]; PARK DONG-SIL [US]; LEB) 22 July 2004 (2004-07-22)	1,4-8, 10-14, 17-19, 22,23
Y	pages 35-37 -----	2,9
X	US 2006/054076 A1 (DWILINSKI ROBERT [PL] ET AL) 16 March 2006 (2006-03-16) paragraphs [0083], [0095] - [0097] -----	1,4,5, 10-12, 14,17, 18,22,23
Y	US 2007/012242 A1 (JURISCH MANFRED [DE] ET AL) 18 January 2007 (2007-01-18) example 1 ----- -/--	2,9

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"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 May 2009	Date of mailing of the international search report 29/05/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Authorized officer Cook, Steven

2

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/008198 A (UNIV CALIFORNIA [US]; JAPAN SCIENCE & TECH AGENCY [JP]; FUJITO KENJI [) 18 January 2007 (2007-01-18) cited in the application -----	
A,P	WO 2008/051589 A (UNIV CALIFORNIA [US]; JAPAN SCIENCE & TECH AGENCY [JP]; HASHIMOTO TADA) 2 May 2008 (2008-05-02) cited in the application -----	
A	WO 2007/117689 A (UNIV CALIFORNIA [US]; JAPAN SCIENCE & TECH AGENCY [JP]; HASHIMOTO TADA) 18 October 2007 (2007-10-18) cited in the application -----	

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/035140

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004061923 A	22-07-2004	AU 2003299899 A1	29-07-2004
		EP 1579486 A1	28-09-2005
		JP 2006513122 T	20-04-2006
		KR 20050087871 A	31-08-2005
US 2006054076 A1	16-03-2006	AU 2002354467 A1	02-12-2003
		AU 2002354485 A1	02-12-2003
		WO 03098757 A1	27-11-2003
		WO 03098708 A1	27-11-2003
		TW 277220 B	21-03-2007
US 2007012242 A1	18-01-2007	US 2009104423 A1	23-04-2009
WO 2007008198 A	18-01-2007	EP 1917382 A1	07-05-2008
		JP 2009500284 T	08-01-2009
WO 2008051589 A	02-05-2008	US 2008102016 A1	01-05-2008
WO 2007117689 A	18-10-2007	EP 2004882 A2	24-12-2008