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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
4 December 2014 (04.12.2014)

(10) **International Publication Number**
WO 2014/191126 A1

(51) **International Patent Classification**:
C30B 7/10 (2006.01) ***C30B 29/40*** (2006.01)

(21) **International Application Number**:
PCT/EP2014/055876

(22) **International Filing Date**:
24 March 2014 (24.03.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
P.404149 30 May 2013 (30.05.2013) PL

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(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, BN, BR, BW, BY, BZ, CA, CH, CL, 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, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, 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, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) **Title**: METHOD FOR OBTAINING MONOCRYSTALLINE GALLIUM-CONTAINING NITRIDE AND MONOCRYSTALLINE GALLIUM-CONTAINING NITRIDE OBTAINED BY THIS METHOD

(57) **Abstract**: The object of the invention is a method for obtaining monocrystalline gallium-containing nitride, from gallium-containing feedstock in the environment of supercritical ammonia-containing solvent with the addition of a mineraliser, containing an element of Group I (IUPAC, 1989), wherein, in an autoclave, two temperature zones are generated, i.e. a dissolution zone of lower temperature, containing feedstock, and, below it, a crystallisation zone of higher temperature, containing at least one seed, a dissolution process of the feedstock and a crystallisation process of the gallium-containing nitride on the at least one seed are carried out, characterised in that at least two additional components are introduced into the process environment, namely: a)an oxygen getter in a molar ratio to ammonia ranging from 0.0001 to 0.2, b)an acceptor dopant in a molar ratio to ammonia not higher than 0.001. The invention also includes monocrystalline gallium-containing nitride, obtained by this method. (20 claims)

Method for Obtaining Monocrystalline Gallium-Containing Nitride and Monocrystalline Gallium-Containing Nitride Obtained by This Method

The object of the invention is a method for obtaining monocrystalline gallium-containing nitride, in the environment of supercritical ammonia-containing solvent with addition of a mineraliser, containing an element of Group I (IUPAC, 1989), wherein, in an autoclave, two temperature zones are generated, i.e. a dissolution zone of lower temperature, containing an feedstock, and, below it, a crystallisation zone of higher temperature, containing at least one seed, a dissolution process of the feedstock and a crystallisation process of the gallium-containing nitride on the at least one seed are carried out. The invention also includes monocrystalline gallium-containing nitride obtained by this method.

From the international patent application No. WO 02/101120 A2, a method for obtaining bulk monocrystalline gallium-containing nitride, and in particular gallium nitride, GaN, by its recrystallization in a supercritical ammonia solution, containing a mineraliser, is known. Document WO 02/101120 A2 comprehensively and exhaustively describes construction of a reactor (high-pressure autoclave) used in this process, as well as an appropriate feedstock, seed, a mineraliser and a temperature-pressure course of the process. The key information disclosed in WO 02/101120 A2 is that gallium nitride has, under these conditions, a negative temperature coefficient of solubility. This means that its solubility decreases along with an increase in temperature. Consequently, in an autoclave, a feedstock is placed above seed, and in recrystallization stage, in the seed zone, a temperature higher than the temperature in the zone, in which the feedstock is located, is maintained. The result of the process conducted this way is dissolution of feedstock and growth of monocrystalline GaN on seed. WO 02/101120 A2 does not mention the use of a metal of Group II (IUPAC, 1989), i.e. an alkali earth metal, and in particular calcium, as an additive for mineraliser or as the mineraliser itself. Mg and Zn are indicated as possible doping elements. Electrical properties of the obtained nitride monocrystals are not described.

The Polish patent application No. P-357706 discloses a complex mineraliser, in the form of alkali metal and alkali earth metal (for example calcium and magnesium are mentioned), used in a molar ratio of 1:500 to 1:5 in relation to alkali metal. The application mentions the possibility of doping the material, but does not specify the amount of particular dopants. Electrical properties of the obtained nitride monocrystals are not described.

In turn, the Polish patent application No. P-357700 discloses a complex mineraliser, in the form of alkali metal and acceptor dopant (for example magnesium, zinc and cadmium are mentioned). The amount of acceptor dopant in relation to the alkali metal or ammonia are generally not specified at the same time. In an embodiment, an admixture in the form of magnesium, used in a molar ratio of 0.05 to the main mineraliser, i.e. to potassium, is disclosed. The application does not mention explicitly the use of calcium in combination with alkali metal as a mineraliser. Electrical properties of the obtained nitride monocrystals are not described.

In the international patent application No. WO 2004/053206 A1, the possibility of using a complex mineraliser, in the form of alkali metal and alkali earth metal, and preferably calcium or magnesium, or in the form of alkali metal and acceptor dopant, such as magnesium, zinc or cadmium, is described again. However, the simultaneous use of alkali metal, calcium and acceptor dopant is not disclosed. Electrical properties of the obtained nitride monocrystals are not described.

The international application No. WO 2005/122232 A1 discloses the use of 0.05 g of Zn or 0.02 g of Mg as an admixture to feedstock which is metallic gallium. This means, that under the process conditions, the molar ratio of Mg or Zn to ammonia, 240 g of which was used, i.e. about 14 mol, is of the order of 10^{-5}. Thereby - according to WO 2005/122232 A1 - a compensated (semi-insulating) material with a resistivity of about 10^{6} Ω cm is obtained. The application does not disclose the use of calcium (or any other oxygen getter) as an admixture to mineraliser. The problem of oxygen content in the crystals obtained is not addressed.

Finally, European application No. EP 2267197 A1, in order to control electrical properties of gallium nitride, and in particular to obtain a compensated (semi-insulating) material, requires to use a mineraliser in the form of alkali metal, and simultaneously with it - an acceptor dopant, specifically magnesium, zinc or manganese, in a molar ratio of at least 0.0001, and most preferably at least 0.001, in relation to ammonia. In case of using zinc or magnesium, p-type material is obtained directly after the process. Only after additional heat treatment (annealing), it becomes a semi-insulating material. In case of using manganese – a semi-insulating material can be obtained directly after the process. The application does not disclose the use of calcium (or any other oxygen getter) as an admixture to mineraliser. The problem of oxygen content in the crystals obtained is not addressed.

So far, it has not been disclosed or suggested, that in this method for obtaining gallium-containing nitride, simultaneously with a mineraliser in the form of alkali metal (metal of Group I, IUPAC, 1989), in a molar ratio of 1 : 200 to 1 : 2 in relation to ammonia, i.e. according to the disclosure of the aforementioned patent applications, to introduce to the process environment, at least two additional components, namely:

a) an oxygen getter in the form of calcium or rare earth element or a combination thereof, in a total molar ratio to ammonia ranging from 0.0001 to 0.2 and

b) acceptor dopants in the form of magnesium, zinc, cadmium, or beryllium, or combinations thereof, in a total molar ratio to ammonia not higher than 0.001.

GaN monocrystals, having been obtained so far without the use of the aforementioned getter and acceptor dopant, are characterised by the concentration of oxygen (unintentionally introduced into the growth environment) at the level of 2×10^{19} cm^{-3} (F. Tuomisto, J.-M. Maki, M. Zając, Vacancy defects in bulk ammonothermal GaN crystals, J. Crystal Growth, 312, 2620 (2010)). Oxygen, present in crystallographic lattice, plays the role of a donor, providing free electrons of similar concentration - in the order of 2×10^{19} cm^{-3} or slightly lower (Tuomisto *et al.*), which makes the considered material highly conductive, with n-type conductivity type. In turn, introduction of the acceptor dopant alone does not change the concentration of oxygen, but allows to change the type of conductivity to p-type, and after appropriate heat treatment, a semi-insulating material with a resistivity of the order of 10^{11} Ω cm can be obtained (patent application EP 2267197 A1). At the same time, Mg acceptor is present therein at the level of up to about 4×10^{19} cm^{-3} (Fig. 2 in application EP 2267197 A1). For a material with a p-type conductivity, by manipulating the concentration of Mg, resistivity and concentration of free holes can be controlled: for the molar ratio of Mg : NH_3 = 0.0001: concentration of holes about 1×10^{18} cm^{-3}, resistivity 9×10^{2} Ω cm; for the molar ratio of Mg : NH_3 = 0.00025: 5×10^{18} cm^{-3} and 8 Ωcm, respectively; for the ratio of Mg : NH_3 = 0.001: 1×10^{19} cm^{-3} and 1.7 Ω cm, respectively (Examples 1 – 4 in application EP 2267197 A1).

Surprisingly, it has been found that simultaneous use of calcium or a rare earth element (or a combination thereof) and an acceptor dopant (or acceptor dopants) provides an advantageous combination of two phenomena. On one hand, it allows to effectively remove oxygen from the obtained crystal, namely, by manipulating the amount of calcium, the concentration of oxygen in the crystal can be continuously changed in the range of about 10^{19} cm^3 to about 10^{18} cm^3. In turn, in the case of rare earth elements – in a wide range of their contents in the reaction environment – a monocrystal with a low oxygen concentration of about 10^{18} cm^3 and less is obtained. On the other hand, acceptor dopants , which are very efficiently incorporated in the obtained monocrystal, compensate the unintentional donors (oxygen), which allows to control electrical properties of the crystal. It appears that, by simultaneously introducing oxygen getters and acceptor dopants into the process environment and by manipulating their composition (relative proportions) and their type, GaN monocrystals of desired electrical parameters (p-type, n-type, semi-insulating material (compensated)) but of higher purity, i.e. of lower concentrations of oxygen and acceptor than those given in EP 2267197 A1, can be obtained. In particular, in order to obtain GaN monocrystals having similar electrical characteristics as in the cited patent application, acceptor dopant is used in the process in a molar ratio (to ammonia) of one or two orders of magnitude lower than in EP 2267197 A1. In a particular case, a material ideally compensated with acceptors, having a very high electrical resistivity, higher than 10^{6} Ω cm, is obtained.

The individual aforementioned components, according to the present invention, can be introduced into the process environment in the elemental (metal) form, as well as in the form of various compounds, such as e.g. azides, amides, imides, amidoimides, hydrides, etc.

These components can be introduced into the environment separately or in combination, wherein in the latter case mixtures of elements or compounds, as well as intermetallic compounds and alloys, can be used. Preferably, but not necessarily, components are introduced into the process environment together with a mineraliser, or in other words a complex mineraliser which, in addition to an alkali metal, contains also the aforementioned oxygen getter and acceptor dopant, is used.

Therefore, it is an object of the present invention to propose a method for obtaining monocrystalline gallium-containing nitride having a reduced oxygen content and desired electrical properties as a result of the use of an oxygen getter and of the simultaneous compensation of unintentional donors (mainly oxygen) with acceptors.

Another object of the invention is to provide such a nitride.

A method for obtaining monocrystalline gallium-containing nitride from gallium-containing feedstock, in the environment of supercritical ammonia-containing solvent with the addition of a mineraliser, containing an element of Group I (IUPAC, 1989), wherein, in an autoclave, two temperature zones are generated, i.e. a dissolution zone of lower temperature, containing feedstock, and, below it, a crystallisation zone of higher temperature, containing at least one seed, a dissolution process of the feedstock and a crystallisation process of the gallium-containing nitride on the at least one seed are carried out, according to the invention is characterised in that at least two additional components are introduced into the process environment, namely:

a) an oxygen getter in a molar ratio to ammonia ranging from 0.0001 to 0.2,

b) an acceptor dopant in a molar ratio to ammonia not higher than 0.001.

Preferably, the oxygen getter is introduced in a molar ratio to ammonia ranging from 0.0005 to 0.05.

Preferably, the oxygen getter is constituted by calcium or a rare earth element, preferably gadolinium or yttrium, or a combination (mixture) thereof.

Preferably, the acceptor dopant is constituted by magnesium, zinc, cadmium or beryllium, or a combination (mixture) thereof.

Preferably, the oxygen getter and the acceptor dopant are introduced in the elemental for, i.e. in the form of metal, or in the form of compound, preferably from the group comprising azides, amides, imides, amidoimides and hydrides, wherein these components are introduced separately or in combination, and in the latter case mixtures of elements or compounds, intermetallic compounds or alloys, being used.

Preferably, the oxygen getter and/or the acceptor dopant are introduced into the process environment together with the mineraliser.

Preferably, the mineraliser contains sodium or potassium, in a molar ratio to ammonia ranging from 0.005 to 0.5.

In a particularly preferred embodiment of the invention, a stoichiometric gallium nitride, GaN, is obtained.

Preferably, the method according to the invention is carried out in an autoclave having a volume higher than 600 cm^3, more preferably higher than 9000 cm^3.

The invention also includes monocrystalline gallium-containing nitride obtained by the above method, containing at least one element of Group I (IUPAC, 1989) in an amount of at least 0.1 ppm, and characterised in that it comprises oxygen at a concentration not higher than 1×10^{19} cm^{-3}, preferably not higher than 3×10^{18} cm^{-3}, and most preferably not higher than 1×10^{18} cm^{-3}.

In a first preferred embodiment, nitride of the invention is an n-type conductive material.

In this case, it contains acceptors selected from magnesium, zinc, cadmium or beryllium with a total concentration not higher than 1×10^{18} cm^{-3}, more preferably not higher than 3×10^{17} cm^{-3}, most preferably not higher than 1×10^{17} cm^{-3}, wherein the ratio of oxygen concentration to the total concentration of acceptors being not lower than 1.2.

Preferably, as an n-type material, nitride of the invention exhibits a concentration of carriers (free electrons) not higher than 7×10^{18} cm, more preferably not higher than 2×10^{18} cm^{-3}, and most preferably not higher than 7×10^{17} cm^{-3}.

In a second preferred embodiment, nitride of the invention is a p-type conductive material.

In this case, it contains acceptors selected from magnesium, zinc, cadmium or beryllium with a total concentration not higher than 2×10^{19} cm^{-3}, more preferably not higher than 6×10^{18} cm^{-3}, most preferably not higher than 2×10^{18} cm^{-3}, the ratio of oxygen concentration to the total concentration of acceptors being not higher than 0.5.

Preferably, as a p-type material, nitride of the invention exhibits a concentration of carriers (free holes) lower than 5×10^{17} cm^{-3}.

In a third preferred embodiment, nitride of the invention is a highly resistive (semi-insulating) material.

In this case, it contains acceptors selected from magnesium, zinc, cadmium or beryllium with a total concentration not higher than 1×10^{19} cm^{-3}, more preferably not higher than 3×10^{18} cm^{-3}, most preferably not higher than 1×10^{18} cm^{-3}, wherein the ratio of oxygen concentration to the total concentration of acceptors ranging from 0.5 to 1.2.

Preferably, as a highly resistive (semi-insulating) material, nitride of the invention has a resistivity higher than $1 \times 10^{5}\ \Omega$ cm, more preferably higher than $1 \times 10^{6}\ \Omega$ cm, and most preferably higher than $1 \times 10^{9}\ \Omega$ cm.

In a particularly preferred embodiment of the invention, nitride of the invention is a stoichiometric gallium nitride, GaN.

The gallium-containing nitride is a chemical compound having in its structure at least a gallium atom and a nitrogen atom. It is therefore at least a two-component compound GaN, a three-component compound AlGaN, InGaN and a four-component compound AlInGaN, preferably containing a substantial amount of gallium at a level higher than the doping level. The composition of other elements with respect to gallium, in the structure of this compound, can be varied to an extent which does not interfere with the ammonia alkaline nature of the crystallisation technique.

The gallium-containing feedstock is gallium-containing nitride or its precursor. As the feedstock, a metallic gallium, GaN obtained by flux methods, HNP method, HVPE method, or a polycrystalline GaN obtained from metallic gallium as a result of reaction in a supercritical ammonia-containing solvent.

The mineraliser is a substance which provides, in the supercritical ammonia-containing solvent, one or more types of ions of alkali metals, and supports dissolution of the feedstock (and gallium-containing nitride).

The supercritical ammonia-containing solvent is a supercritical solvent, consisting at least of ammonia in which one or more types of alkali metal ions are contained, the said ions supporting dissolution of gallium-containing nitride. The supercritical ammonia-containing solvent may also contain derivatives of ammonia and/or their mixtures, in particular hydrazine.

Preferred Embodiments of the Invention

Example 1. Obtaining of doped GaN (Ca : NH_3 = 0.0005, Mg : NH_3 = 0.000005, Na : NH_3 = 0.04)

In a high-pressure autoclave with a volume of 600 cm^3, in a dissolution zone, as the feedstock, 107.8 g (about 1.3 mol) of polycrystalline GaN with the addition of 0.22 g of Ca (5.6 mmol) and 1.3 mg of Mg (0.05 mmol) was placed. Into the autoclave, 10.34 g (about 449 mmol) of metallic sodium having a purity of 4N was also introduced.

As the seed, 18 plates of monocrystalline gallium nitride obtained by HVPE method or by crystallisation from supercritical ammonia-containing solution, oriented perpendicularly to c-axis of monocrystal, with a diameter of about 25 mm (1 inch) and a thickness of about 500 μm each. The seed were placed in a crystallisation zone of the autoclave.

Then, the autoclave was filled with ammonia (5N) in the amount of 191 g (about 11.2 mol), closed and introduced to a set of furnaces.

The dissolution zone was heated at a rate of about 0.5°C/min) to 450°C. At this time, the crystallisation zone was not heated. After reaching, in the dissolution zone, a predetermined temperature of 450°C, i.e. after about 15 hours from the beginning of the process, the temperature in the crystallisation zone was about 170°C. This temperature distribution had been maintained in the autoclave for 4 days. At this time, a partial carrying of gallium to the solution and a complete conversion of undissolved gallium to polycrystalline GaN occurred. Then, the temperature in the crystallisation zone was raised (a rate of about 0.1°C/min) to 550°C, and the temperature in the dissolution zone remained unchanged. The pressure inside the autoclave was about 410 MPa. The result of this temperature distribution was emergence of convection between zones in the autoclave, and consequently - of chemical transport of gallium nitride from the (upper) dissolution zone to the (lower) crystallisation zone, where it was deposited on seed. The obtained temperature distribution (i.e. 450°C in the dissolution zone and 550°C in the crystallisation zone) was maintained for the next 56 days (to the end of the process).

As a result of the process, partial dissolution of the feedstock (i.e. polycrystalline GaN) in the dissolution zone and growth of monocrystalline gallium nitride on seed, (on each seed) about 1.75 mm (measured in the direction of c-axis of the monocrystal), occurred. As a result of this process, an n-type conductive material with a concentration of free electrons of 4.8×10^{18} cm^{-3} and with a resistivity of 2×10^{-2} Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 9.0×10^{18} cm^{-3}, the concentration of Mg – 9.5×10^{16} cm^{-3}.

Example 2. Obtaining of doped GaN (Ca : NH_3 = 0.005; Mg : NH_3 = 0.000005, K : NH_3 = 0.08)

In a high-pressure autoclave with a volume of 9300 cm^3, in a dissolution zone, as the feedstock, 1.3 kg (about 16.3 mol) of polycrystalline GaN with the addition of 37.6 g of Ca (940 mmol) and 23 mg of Mg (0.9 mmol) was placed. Into the autoclave, 588 g (about 15 mol) of metallic potassium having a purity of 4N was also introduced.

As the seed, 60 plates of monocrystalline gallium nitride obtained by HVPE method or by crystallisation from supercritical ammonia-containing solution, oriented perpendicularly to c-axis of the monocrystal, with a diameter of about 50 mm (2 inches) and a thickness of about 1500 µm each. The seed were placed in a crystallisation zone of the autoclave.

Then, the autoclave was filled with ammonia (5N) in the amount of 3.2 kg (about 188 mol), closed and introduced to a set of furnaces.

The dissolution zone was heated (a rate of about 0.5°C/min) to 550°C. At this time, the dissolution zone was not heated. After reaching, in the dissolution zone, a predetermined temperature of 450°C, i.e. after about 15 hours from the beginning of the process, the temperature in the crystallisation zone was about 170°C. This temperature distribution had been maintained in the autoclave for 4 days. At this time, a partial carrying of gallium to the solution and a complete conversion of undissolved gallium to polycrystalline GaN occurred. Then, the temperature in the crystallisation zone was raised (a rate of about 0.1°C/min) to 550°C, and the temperature in the dissolution zone remained unchanged. The pressure inside the autoclave was about 410 MPa. The result of this temperature distribution was emergence of convection between zones in the autoclave, and consequently – of chemical transport of gallium nitride from the (upper) dissolution zone to the (lower) crystallisation zone, where it was deposited on seed. The obtained temperature distribution (i.e. 450°C in the dissolution zone and 550°C in the crystallisation zone) was maintained for the next 56 days (to the end of the process).

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.8 mm (measured in the direction of c-axis of the monocrystal) was obtained. A conductive material of n-type conductivity and with a resistivity of 5×10^{-2} Ω cm and with a concentration of free electrons of 1.2×10^{18} cm^{-3} was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 9.4×10^{17} cm^{-3}, the concentration of Mg – 9.0×10^{16} cm^{-3}.

Example 3. Obtaining of doped GaN (Ca : NH_3 = 0.05, Mg : NH_3 = 0.000005, Na : NH_3 = 0.08)

The same procedure as in Example 2, with the exception that, as solid substrates, 1.1 kg of metallic Ga (16.3 mol), 376 g of Ca (about 9.4 mol), 23 mg of Mg (0.9 mmol), 345 g of Na (15 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.6 mm (measured in the direction of c-axis of the monocrystal) was obtained. A conductive n-type material with a resistivity of 8×10^{-2} Ω cm and with a concentration of electrons of 1.1×10^{18} cm^{-3} was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 1.3×10^{18} cm^{-3} (saturation of oxygen level together with the increasing concentration of Ca), the concentration of Mg – 5×10^{16} cm^{-3}.

Example 4. Obtaining of doped GaN (Ca : NH_3 = 0.005, Mg : NH_3 = 0.00002, Na : NH_3 = 0.04)

The same procedure as in Example 1, with the exception that, as solid substrates, 89.8 g of metallic Ga (1.29 mol), 2.25 g of Ca (56.2 mmol), 5.4 mg of Mg (about 0.22 mmol), 10.4 g of Na (0.45 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.73 mm (measured in the direction of c-axis of the monocrystal) was obtained. A highly resistive material with a resistivity of > 10^6 Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 8.2×10^{17} cm^{-3}, the concentration of Mg – 1.1×10^{18} cm^{-3}.

Example 5. Obtaining of doped GaN (Ca : NH_3 = 0.005, Mg : NH_3 = 0.00005, Na : NH_3 = 0.04)

The same procedure as in Example 1, with the exception that, as solid substrates, 89.8 g of metallic Ga (1.29 mol), 2.25 g of Ca (56.2 mmol), 13 mg of Mg (about 0.56 mmol), 10.4g of Na (0.45 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.79 mm (measured in the direction of axis *c* of the monocrystal) was obtained. A material of p-type conductivity and with a concentration of carriers (free holes) of 3×10^{16} cm^{-3} and with a resistivity of 2×10^1 Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 1.3×10^{18} cm^{-3}, the concentration of Mg – 5×10^{18} cm^{-3}.

Example 6. Obtaining of doped GaN (Ca : NH_3 = 0.005; Mg : NH_3 = 0.0002, K : NH_3 = 0.12)

The same procedure as in Example 1, with the exception that, as solid substrates, 107.8 g of polycrystalline GaN (1.3 mol), 2.25 g of Ca (56.2 mmol), 0.05 g of Mg (about 2.25 mmol), 52.7 g of K (1.3 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.7 mm (measured in the direction of c-axis of the monocrystal) was obtained. A material of p-type conductivity and with a concentration of carriers (free holes) of 1.8×10^{17} cm^{-3} and with a resistivity of 7×10^1 Ω cm was obtained.

The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 1.5×10^{18} cm^{-3}, the concentration of Mg – 8×10^{18} cm^{-3}.

Example 7. Obtaining of doped GaN (Gd : NH_3 = 0.001, Mg : NH_3 = 0.000005, Na : NH_3 = 0.04)

The same procedure as in Example 1, with the exception that, as solid substrates, 89.8 g of metallic Ga (1.3 mol), 1.8 g of Gd (11.2 mmol), 1.3 mg of Mg (about 0.056 mmol), 10.3 g of Na (0.45 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.9 mm (measured in the direction of c-axis of the monocrystal) was obtained. An n-type conductive material with a concentration of free electrons of 2×10^{17} cm^{-3} and with a resistivity of 6×10^{-2} Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 1.2×10^{18} cm^{-3}, the concentration of Mg – 5×10^{17} cm^{-3}.

Example 8. Obtaining of doped GaN (Gd : NH_3 = 0.001, Mg : NH_3 = 0.00002, K : NH_3 = 0.08)

The same procedure as in Example 1, with the exception that, as solid substrates, 107.8 g of polycrystalline GaN (1.3 mol), 1.8 g of Gd (11.2 mmol), 5 mg of Mg (about 0.22 mmol) and 35.2 g of K (0.9 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.6 mm (measured in the direction of c-axis of the monocrystal) was obtained. A highly resistive material with a resistivity of $> 1 \times 10^{6}$ Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 8×10^{17} cm^{-3}, the concentration of Mg – 1.2×10^{18} cm^{-3}.

Example 9. Obtaining of doped GaN (Gd : NH_3 = 0.0075; Ca : NH_3 = 0.0025; Mg : NH_3 = 0.00015; Zn : NH_3 = 0.00005; K : NH_3 = 0.12)

The same procedure as in Example 1, with the exception that, as solid substrates, 107.8 g of polycrystalline GaN (1.3 mol), 13.2 g of Gd (84.3 mmol), 1.1 g of Ca (28.1 mmol), 41 mg of Mg (about 1.7 mmol), 36 mg of Zn (0.56 mmol) and 52.7 g of K (1.35 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.65 mm (measured in the direction of c-axis of the monocrystal) was obtained. A p-type material with a resistivity of 1.5×10^{1} Ω cm and with a concentration of carriers (free holes) of 7×10^{16} cm^{-3} was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 9×10^{17} cm^{-3}, the concentration of Mg - 4.5×10^{18} cm^{-3}, and the concentration of Zn – 1.5×10^{18} cm^{-3}.

Example 10. Obtaining of doped GaN (Gd : NH_3 = 0.001; Zn : NH_3 = 0.000005; Na : NH_3 = 0.04)

The same procedure as in Example 2, with the exception that, as solid substrates, 1.1 kg of metallic Ga (16.3 mol), 29.5 g of Gd (188 mmol) and 61 mg of Zn (about 0.9 mmol), and 173 g of Na (7.5 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.72 mm (measured in the direction of c-axis of the monocrystal) was obtained. An n-type material with a concentration of free electrons of 6×10^{17} cm^{-3}, with a resistivity of 3×10^{-2} Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 1.1×10^{18} cm^{-3}, the concentration of Zn – 1.2×10^{17} cm^{-3}.

Example 11. Obtaining of doped GaN (Gd : NH_3 = 0.0075; Y : NH3 = 0.0025; Zn : NH_3 = 0.00002; K : NH_3 = 0.04)

The same procedure as in Example 1, with the exception that, as solid substrates, 107.8 g of polycrystalline GaN (1.3 mol), 13.2 g of Gd (about 84.3 mmol), 2.5 g of Y (about 28.1 mmol), 14 mg of Zn (0.22 mmol) and 17.6 g of K (0.45 mmol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.8 mm (measured in the direction of c-axis of the monocrystal) was obtained. An n-type material with a concentration of free electrons of 1×10^{17} cm^{-3}, with a resistivity of 8×10^{-2} Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 9×10^{17} cm^{-3}, the concentration of Zn – 6×10^{17} cm^{-3}.

Example 12. Obtaining of doped GaN (Gd : NH_3 = 0.001; Zn : NH_3 = 0.00005; Na : NH_3 = 0.08)

The same procedure as in Example 1, with the exception that, as solid substrates, 89.8 g of metallic Ga (1.3 mol), 1.8 g of Gd (11.2 mmol), 36 mg of Zn (about 0.5 mmol), and 20.6 g of Na (0.9 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.76 mm (measured in the direction of c-axis of the monocrystal) was obtained. A highly resistive material with a resistivity of > 10^6 Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 9.8×10^{17} cm^{-3}, the concentration of Zn - 1.2×10^{18} cm^{-3}.

Example 13. Obtaining of doped GaN (Gd : NH_3 = 0.001; Zn : NH_3 = 0.0002; Na : NH_3 = 0.08)

The same procedure as in Example 1, with the exception that, as solid substrates, 107.8 g of polycrystalline GaN (1.3 mol), 1.8g of Gd (11.2 mmol), 0.14 g of Zn (about 2.2 mmol) and 20.6 g of Na (0.9 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.68 mm (measured in the direction of c-axis of the monocrystal) was obtained. A p-type material with a concentration of free carriers (holes) of 1×10^{16} cm^{-3} and with a resistivity of 2×10^{2} Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 8.2×10^{17} cm^{-3}, the concentration of Zn - 4.2×10^{18} cm^{-3}.

Example 14. Obtaining of doped GaN (Y : NH_3 = 0.01; Zn : NH_3 = 0.000005, K : NH_3 = 0.04)

The same procedure as in Example 2, with the exception that, as solid substrates, 1.1 kg of metallic Ga (16.3 mol), 167 g of yttrium (Y) (1.9 mol), 60 mg of Zn (0.9 mmol) and 294 g (7.5 mol) of K were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.8 mm (measured in the direction of c-axis of the monocrystal) was obtained. An n-type material with a concentration of free carriers (electrons) of 2.3×10^{18} cm^{-3} and with a resistivity of 8×10^{-2} Ω cm was obtained.

The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 3×10^{18} cm^{-3}, the concentration of Zn – 2.1×10^{17} cm^{-3}.

Example 15. Obtaining of doped GaN (Y : NH_3 = 0.01; Zn : NH_3 = 0.00005, Na : NH_3 = 0.08)

The same procedure as in Example 1, with the exception that, as solid substrates, 89.8 g of metallic Ga (1.3 mol), 10 g of yttrium (Y) (112 mmol), 36 mg of Zn (0.56 mmol), 20.7 g of Na (0.9 mol) were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.7 mm (measured in the direction of c-axis of the monocrystal) was obtained. A highly resistive material with a resistivity of > 10^6 Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS), is 3.2×10^{18} cm^{-3}, the concentration of Zn - 4×10^{18} cm^{-3}.

Example 16. Obtaining of doped GaN (Y : NH_3 = 0.01; Zn : NH3 = 0.00015; Mg : NH_3 = 0.00005; K : NH_3 = 0.12)

The same procedure as in Example 1, with the exception that, as solid substrates, 89.8 g of metallic Ga (1.3 mol), 10 g of yttrium (Y) (112 mmol), 0.11 g of Zn (1.7 mmol), 14 mg of Mg (0.56 mmol), 52.7 g of K were used.

As a result of the process, a layer of GaN (on each seed) with a thickness of about 1.75 mm (measured in the direction of c-axis of the monocrystal) was obtained. A p-type material with a concentration of free carriers (holes) of 2×10^{16} cm^{-3} and with a resistivity of 3×10^1 Ω cm was obtained. The concentration of oxygen, measured by secondary ion mass spectroscopy (SIMS),is 2.5×10^{18} cm^{-3}, the concentration of Zn – 5.7×10^{18} cm^{-3}, and the concentration of Mg – 1.8×10^{18} cm^{-3}.

Claims

1. A method for obtaining monocrystalline gallium-containing nitride from gallium-containing feedstock, in the environment of supercritical ammonia-containing solvent with the addition of a mineraliser, containing an element of Group I (IUPAC, 1989), wherein, in an autoclave, two temperature zones are generated, i.e. a dissolution zone of lower temperature, containing feedstock, and, below it, a crystallisation zone of higher temperature, containing at least one seed a dissolution process of the feedstock and a crystallisation process of the gallium-containing nitride on the at least one seed are carried out, **characterised in that** at least two additional components are introduced into the process environment, namely:
   a) an oxygen getter in a molar ratio to ammonia ranging from 0.0001 to 0.2;
   b) an acceptor dopant in a molar ratio to ammonia not higher than 0.001.
2. The method according to claim 1, **characterised in that** the oxygen getter is introduced in a molar ratio to ammonia ranging from 0.0005 to 0.05.
3. The method according to claim 1 or 2, **characterised in that** the oxygen getter is constituted by calcium or a rare earth element, preferably gadolinium or yttrium, or a combination thereof.
4. The method according to claim 1, 2 or 3 **characterised in that** the acceptor dopant is constituted by magnesium, zinc, cadmium or beryllium, or a combination thereof.
5. The method according to claim 1, 2, 3 or 4 **characterised in that** the oxygen getter and the acceptor dopant are introduced in the elemental form, i.e. in the form of metal, or in the form of compound, preferably from the group comprising azides, amides, imides, amidoimides and hydrides, wherein these components are introduced separately or in combination, and in the case of introducing them in combination, mixtures of elements or compounds, intermetallic compounds or alloys, are used.

6. The method according to any one of the preceding claims, **characterised in that** the oxygen getter and/or the acceptor dopant are introduced into the process environment together with the mineraliser.

7. The method according to any one of the preceding claims, **characterised in that** the mineraliser contains sodium or potassium, in a molar ratio to ammonia ranging from 0.005 to 0.5.

8. The method according to any one of the preceding claims, **characterised in that** a stoichiometric gallium nitride, GaN, is obtained.

9. The method according to any one of the preceding claims, **characterised in that** it is carried out in an autoclave having an internal volume higher than 600 cm^3, more preferably higher than 9000 cm^3.

10. Monocrystalline gallium-containing nitride, obtained by the method according to any one of the preceding claims, containing at least one element of Group I (IUPAC, 1989) in an amount of at least 0.1 ppm, **characterised in that** it contains oxygen in a concentration not higher than 1×10^{19} cm^{-3}, preferably not higher than 3×10^{18} cm^{-3}, and most preferably not higher than 1×10^{18} cm^{-3}.

11. The nitride according to claim 10, **characterised in that** it is an n-type conductive material.

12. The nitride according to claim 11, **characterised in that** it contains acceptors selected from magnesium, zinc, cadmium or beryllium with a total concentration not higher than 1×10^{18} cm^{-3}, more preferably not higher than 3×10^{17} cm^{-3}, most preferably not higher than 1×10^{17} cm^{-3}, wherein the ratio of oxygen concentration to the total concentration of acceptors being not lower than 1.2.

13. The nitride according to claim 11 or 12, **characterised in that** it exhibits a concentration of carriers (free electrons) not higher than 7×10^{18} cm^{-3}, more preferably not higher than 2×10^{18} cm^{-3}, and most preferably not higher than 7×10^{17} cm^{-3}.

14. The nitride according to claim 10, **characterised in that** it is a p-type conductive material.

15. The nitride according to claim 14, **characterised in that** it contains acceptors selected from magnesium, zinc, cadmium or beryllium with a total concentration not higher than 2 × 10^{19} cm^{-3}, more preferably not higher than 6 × 10^{18} cm^{-3}, most preferably not higher than 2 × 10^{18} cm^{-3}, wherein the ratio of oxygen concentration to the total concentration of acceptors being not higher than 0.5.

16. The nitride according to claim 14 or 15, **characterised in that** it exhibits a concentration of carriers (free holes) lower than 5 × 10^{17} cm^{-3}.

17. The nitride according to claim 10, **characterised in that** it is a highly resistive (semi-insulating) material.

18. The nitride according to claim 17, **characterised in that** it contains acceptors selected from magnesium, zinc, cadmium or beryllium with a total concentration not higher than 1 × 10^{19} cm^{-3}, more preferably not higher than 3 × 10^{18} cm^{-3}, most preferably not higher than 1 × 10^{18} cm^{-3}, the ratio of oxygen concentration to the total concentration of acceptors ranging from 0.5 to 1.2.

19. The nitride according to claim 17 or 18, **characterised in that** it has a resistivity higher than 1 × 10^{5} Ω cm, more preferably higher than 1 × 10^{6} Ω cm, and most preferably higher than 1 × 10^{9} Ω cm.

20. The nitride according to any one of the preceding claims 10 to 19, **characterised in that** it is a stoichiometric gallium nitride GaN.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/055876

A. CLASSIFICATION OF SUBJECT MATTER
INV. C30B7/105 C30B29/406 C30B7/10 C30B29/40
ADD.

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 practicable, search terms used)

EPO-Internal, WPI Data

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☒ 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 application or patent 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 27 June 2014	Date of mailing of the international search report 17/07/2014
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 Aliouane, Nadir

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/055876

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/055876

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(19) 中华人民共和国国家知识产权局

(12) 发明专利申请

(10) **申请公布号** CN 105556006 A
(43) **申请公布日** 2016.05.04

(21) **申请号** 201480031120.6

(22) **申请日** 2014.03.24

(30) **优先权数据**
P.404149 2013.05.30 PL

(85) **PCT国际申请进入国家阶段日**
2015.11.30

(86) **PCT国际申请的申请数据**
PCT/EP2014/055876 2014.03.24

(87) **PCT国际申请的公布数据**
WO2014/191126 EN 2014.12.04

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(51) **Int.Cl.**
C30B 29/40(2006.01)
C30B 7/10(2006.01)

权利要求书2页　说明书8页

(54) **发明名称**

获得单晶含镓氮化物的方法以及由该方法获得的单晶含镓氮化物

(57) **摘要**

本发明的目的在于在添加有含第I族(IUPAC,1989)元素的矿化剂的超临界含氨溶剂的环境下由含镓原料获得单晶含镓氮化物的方法，其中，在高压釜中产生两个温度区域，即，温度较低的溶解区域和其下方的温度较高的结晶区域，所述溶解区域包含原料，所述结晶区域包含至少一个晶种，进行原料的溶解过程和含镓氮化物在至少一个晶种上的结晶过程，所述方法的特征在于向过程环境中引入至少两种另外的组分，即：a) 吸氧剂，其相对于氨的摩尔比为0.0001至0.2；b) 受主掺杂剂，其相对于氨的摩尔比不大于0.001。本发明还包括通过此方法获得的单晶含镓氮化物。

1.一种用于在添加有含第I族(IUPAC,1989)元素的矿化剂的超临界含氨溶剂的环境下由含镓原料获得单晶含镓氮化物的方法,其中,在高压釜中产生两个温度区域,即包含原料的温度较低的溶解区域和其下方的包含至少一个晶种的温度较高的结晶区域,进行原料的溶解过程和含镓氮化物在至少一个晶种上的结晶过程,所述方法的特征在于,向过程环境中引入至少两种额外的组分,即:

a)吸氧剂,其相对于氨的摩尔比为0.0001至0.2;

b)受主掺杂剂,其相对于氨的摩尔比不大于0.001。

2.根据权利要求1所述的方法,其特征在于,以相对于氨为0.0005至0.05的摩尔比引入所述吸氧剂。

3.根据权利要求1或2所述的方法,其特征在于,所述吸氧剂由钙或稀土元素构成,优选由钆或钇、或其组合构成。

4.根据权利要求1、2或3所述的方法,其特征在于,所述受主掺杂剂由镁、锌、镉或铍、或者其组合构成。

5.根据权利要求1、2、3或4所述的方法,其特征在于,以单质形式即金属形式、或以化合物形式引入所述吸氧剂和所述受主掺杂剂,所述化合物优选选自叠氮化物、酰胺、酰亚胺、酰胺酰亚胺以及氢化物,其中将这些组分单独地引入或组合地引入,并且在将这些组分组合地引入的情况下,使用单质的混合物或化合物的混合物、金属间化合物或者合金。

6.根据前述权利要求中任一项所述的方法,其特征在于,将所述吸氧剂和/或所述受主掺杂剂与矿化剂一起引入到过程环境中。

7.根据前述权利要求中任一项所述的方法,其特征在于,所述矿化剂以相对于氨为0.005至0.5的摩尔比包含钠或钾。

8.根据前述权利要求中任一项所述的方法,其特征在于,获得化学计量比的氮化镓GaN。

9.根据前述权利要求中任一项所述的方法,其特征在于,在内体积大于600cm^3、更优选大于9000cm^{3}的高压釜中进行所述方法。

10.一种通过根据前述权利要求中任一项所述的方法获得的单晶含镓氮化物,其以至少0.1ppm的量包含第I族(IUPAC,1989)的至少一种元素,其特征在于,所述单晶含镓氮化物以不高于1×10^{19}cm^{-3}、优选不高于3×10^{18}cm^{-3}、最优选不高于1×10^{18}cm^{-3}的浓度包含氧。

11.根据权利要求10所述的氮化物,其特征在于,所述氮化物是n型导电材料。

12.根据权利要求11所述的氮化物,其特征在于,所述氮化物以不高于1×10^{18}cm^{-3}、更优选不高于3×10^{17}cm^{-3}、最优选不高于1×10^{17}cm^{-3}的总浓度包含选自镁、锌、镉或铍的受主,其中氧浓度与受主总浓度的比不低于1.2。

13.根据权利要求11或12所述的氮化物,其特征在于,所述氮化物显示出不高于7×10^{18}cm^{-3}、更优选不高于2×10^{18}cm^{-3}、最优选不高于7×10^{17}cm^{-3}的载流子(自由电子)的浓度。

14.根据权利要求10所述的氮化物,其特征在于,所述氮化物是p型导电材料。

15.根据权利要求14所述的氮化物,其特征在于,所述氮化物以不高于2×10^{19}cm^{-3}、更优选不高于6×10^{18}cm^{-3}、最优选不高于2×10^{18}cm^{-3}的总浓度包含选自镁、锌、镉或铍的受主,其中氧浓度与受主总浓度的比不高于0.5。

16.根据权利要求14或15所述的氮化物,其特征在于,所述氮化物显示出低于5×

10^{17}cm^{-3}的载流子(自由空穴)的浓度。

17.根据权利要求10所述的氮化物,其特征在于,所述氮化物是高电阻(半绝缘)材料。

18.根据权利要求17所述的氮化物,其特征在于,所述氮化物以不高于1×10^{19}cm^{-3}、更优选不高于3×10^{18}cm^{-3}、最优选不高于1×10^{18}cm^{-3}的总浓度包含选自镁、锌、镉或铍的受主,氧浓度与受主总浓度的比为0.5至1.2。

19.根据权利要求17或18所述的氮化物,其特征在于,所述氮化物具有大于1×10^{5}Ω·cm、更优选大于1×10^{6}Ω·cm、最优选大于1×10^{9}Ω·cm的电阻率。

20.根据前述权利要求10至19中任一项所述的氮化物,其特征在于,所述氮化物是化学计量比的氮化镓GaN。

获得单晶含镓氮化物的方法以及由该方法获得的单晶含镓氮化物

[0001]　本发明的目的是一种在添加了含有第I族(IUPAC,1989)元素的矿化剂的超临界含氨溶剂的环境下获得单晶含镓氮化物的方法，其中，在高压釜中产生两个温度区域，即温度较低的溶解区域和其下方的温度较高的结晶区域，所述溶解区域包含原料，所述结晶区域包含至少一个晶种，进行原料的溶解过程和含镓氮化物在至少一个晶种上的结晶过程。本发明还包括通过此方法获得的单晶含镓氮化物。

[0002]　由国际专利申请第WO 02/101120 A2号已知一种通过在含矿化剂的超临界氨溶液中再结晶来获得块状单晶含镓氮化物、尤其是氮化镓GaN的方法。文献WO 02/101120 A2全面且详尽地描述了在该工艺中使用的反应器(高压釜)的结构以及合适的原料、晶种、矿化剂以及工艺的温度-压力过程。在WO 02/101120 A2中公开的关键信息是氮化镓在这些条件下具有负的溶解度温度系数。这意味着其溶解度随温度上升而下降。因此，在高压釜中，将原料放置在晶种上方，并且在再结晶阶段，在晶种区域维持比原料所在的区域的温度高的温度。以该方式进行的工艺的结果是原料溶解且单晶GaN在晶种上生长。WO 02/101120 A2没有提到使用II族(IUPAC,1989)金属即碱土金属，特别是钙，作为用于矿化剂的添加剂或作为矿化剂本身。其指出Mg和Zn为可能的掺杂元素。没有描述获得的氮化物单晶的电性能。

[0003]　波兰专利申请第P-357706号公开了一种为碱金属和碱土金属(例如提到了钙和镁)形式的复合矿化剂，所述碱土金属以相对于所述碱金属为1:500至1:5的摩尔比使用。该申请提到了使材料掺杂的可能性，但是没有详细说明具体的掺杂剂的量。没有描述获得的氮化物单晶的电性能。

[0004]　进而，波兰专利申请第P-357700号公开了一种为碱金属与受主掺杂剂(例如提到了镁、锌及镉)形式的复合矿化剂。没有同时具体说明受体掺杂剂相对于碱金属或氨的量。在实施方案中，公开了镁形式的掺和剂，其以相对于主要矿化剂即相对于钾为0.05的摩尔比使用。申请没有明确地提到将钙与碱金属组合使用作为矿化剂。没有描述获得的氮化物单晶的电性能。

[0005]　在国际专利申请第WO 2004/053206 A1号中，也描述了使用为碱金属与碱土金属、优选钙或镁形式的复合矿化剂，或者碱金属与受主掺杂剂例如镁、锌或镉形式的复合矿化剂。然而，没有公开同时使用碱金属、钙及受主掺杂剂。没有描述获得的氮化物单晶的电性能。

[0006]　国际申请第WO 2005/122232 A1号公开了使用0.05g的Zn或0.02g的Mg作为原料的掺和剂，所述原料为金属镓。这意味着，在工艺条件下，Mg或Zn相对于氨的摩尔比约为10^{-5}的量级，所述氨使用了240g即约14mol。因此，根据WO 2005/122232 A1，获得了电阻率为约10^{6} Ω·cm的补偿(半绝缘)材料。申请没有公开使用钙(或任何其他吸氧剂)作为矿化剂的掺和剂。没有解决获得的晶体中的氧含量的问题。

[0007]　最后，欧洲申请第EP 2267197 A1号，为了控制氮化镓的电性能且尤其是为了获得补偿(半绝缘)材料，需要以至少0.0001、最优选至少0.001的相对于氨的摩尔比使用为碱金属形式的矿化剂，并与其同时地使用受主掺杂剂，具体为镁、锌或锰掺杂剂。在使用锌或镁

的情况下，在工艺后直接获得p型材料。只有在另外的加热处理(退火)后，它才成为半绝缘材料。在使用锰的情况下，在工艺后能够直接获得半绝缘材料。申请没有公开使用钙(或任何其他吸氧剂)作为矿化剂的掺和剂。没有解决获得的晶体中的氧含量的问题。

[0008] 目前为止，根据前述专利申请的公开内容，没有公开或建议在该用于获得含镓氮化物的方法中，以相对于氨为1:200至1:2的摩尔比与碱金属(第I族金属，IUPAC，1989)形式的矿化剂同时地将至少两种额外的组分引入过程环境，即：

[0009] a)为钙或稀土元素或其组合的形式的吸氧剂，其相对于氨的总摩尔比为0.0001至0.2；和

[0010] b)未镁、锌、镉或铍或其组合的形式的受主掺杂剂，其相对于氨的总摩尔比不大于0.001。

[0011] 目前为止，在不使用前述吸氧剂和受主掺杂剂的情况下获得的GaN单晶的特征在于，氧(非有意地引入生长环境中)浓度的水平为$2\times10^{19}cm^{-3}$(F.Tuomisto,J.-M.Maki,M.Zajac,Vacancy defects in bulk ammonothermal GaN crystals,J.Crystal Growth,312,2620(2010))。晶格中存在的氧起施主作用，其提供约$2\times10^{19}cm^{-3}$或略低的相似浓度的自由电子(Tuomisto等)，这使得所涉及的材料为高导电性的，为n型导电类型。此外，受主掺杂剂的单独引入不改变氧的浓度，但是能够使导电类型变为p型，并且在适当的加热处理后，能够得到电阻率为$10^{11}\Omega\cdot cm$量级的半绝缘材料(专利申请EP 2267197A1)。同时，其中以高达约$4\times10^{19}cm^{-3}$的水平存在Mg受主(申请EP 2267197A1的图2)。对于具有p型导电性的材料，能够通过操纵Mg的浓度从而控制电阻率和空穴浓度：对于摩尔比$Mg:NH_3=0.0001$：空穴的浓度为约$1\times10^{18}cm^{-3}$，电阻率为$9\times10^{2}\Omega\cdot cm$；对于摩尔比$Mg:NH_3=0.00025$，空穴的浓度和电阻率分别为$5\times10^{18}cm^{-3}$和$8\Omega\cdot cm$；对于摩尔比$Mg:NH_3=0.001$：空穴的浓度和电阻率分别为$1\times10^{19}cm^{-3}$和$1.7\Omega\cdot cm$(申请EP 2267197A1的实施例1至4)。

[0012] 出人意料地，已经发现将钙或稀土元素(或其组合)与受主掺杂剂同时使用提供了两种现象的有利组合。一方面，能够有效地从获得的晶体中移除氧，即，通过操纵钙的量，能够使晶体中氧的浓度从约$10^{19}cm^{3}$至约$10^{18}cm^{3}$连续地改变。此外，在反应环境中以大范围的含量使用稀土元素的情况下，获得具有为约$10^{18}cm^{3}$或更低的低的氧浓度的单晶。另一方面，非常有效地并入到获得的单晶中的受体掺杂剂补偿了非有意的施主(氧)，这使得能够控制晶体的电性能。看起来，通过向工艺环境中同时引入吸氧剂和受主掺杂剂，以及通过操纵它们的组成(相对比例)和它们的类型，能够获得具有期望的电学参数(p型、n型、半绝缘材料(补偿))的GaN单晶，但所述GaN单晶具有较高的纯度，即具有比EP 2267197 A1所给出氧和受主浓度更低的氧和受主浓度。特别地，为了获得具有与引用的专利申请相似的电特性的GaN单晶，在工艺中以比EP 2267197 A1中低一或两个数量级的摩尔比(相对于氨)使用受体掺杂剂。在具体情况中，获得了理想地由受主补偿的材料，所述材料具有比$10^{6}\Omega\cdot cm$更高的非常高的电阻率。

[0013] 根据本发明，能够以单质(金属)形式、以及以各种化合物例如叠氮化物、酰胺、酰亚胺、酰胺酰亚胺、氢化物等的形式向工艺环境中引入各个前述组分。

[0014] 可以单独地或者组合地将这些组分引入环境中，其中，在组合引入的情况下，可以使用单质的混合物或化合物的混合物、以及金属间化合物和合金。优选地，但非必须地，将组分与矿化剂一起引入工艺环境中，或者换言之，使用除碱金属外还包含前述吸氧剂和受

体掺杂剂的复合矿化剂。

[0015] 因此，本发明的目的在于提出获得单晶含镓氮化物的方法，所述单晶含镓氮化物由于使用吸氧剂且同时用受主补偿非有意的施主（主要是氧）而具有减少的氧含量和期望的电性能。

[0016] 本发明的另一个目的在于提供这样的氮化物。

[0017] 一种在添加有含第I族（IUPAC，1989）元素的矿化剂的超临界含氨溶剂的环境下由含镓原料获得单晶含镓氮化物的方法，其中，在高压釜中产生两个温度区域，即温度较低的溶解区域和其下方的温度较高的结晶区域，所述溶解区域包含原料，所述结晶区域包含至少一个晶种，进行原料的溶解过程和含镓氮化物在至少一个晶种上的结晶过程，根据本发明，所述方法的特征在于向过程环境中引入至少两种额外的组分，即：

[0018] a）吸氧剂，其相对于氨的摩尔比为0.0001至0.2；

[0019] b）受主掺杂剂，其相对于氨的摩尔比不大于0.001。

[0020] 优选地，以相对于氨为0.0005至0.05的摩尔比引入吸氧剂。

[0021] 优选地，吸氧剂由钙或稀土元素、优选钆或钇、或其组合构成。

[0022] 优选地，受主掺杂剂由镁、锌、镉或铍、或其组合（混合物）构成。

[0023] 优选地，以单质即以金属形式或以化合物形式引入所述吸氧剂与所述受主掺杂剂，所述化合物优选选自叠氮化物、酰胺、酰亚胺、酰胺酰亚胺以及氢化物，其中，将这些组分单独地或组合地引入，并且在组合引入的情况下，使用单质的混合物或化合物的混合物、金属间化合物或者合金。

[0024] 优选地，将吸氧剂和/或受主掺杂剂与矿化剂一起引入过程环境。

[0025] 优选地，矿化剂以相对于氨为0.005至0.5的摩尔比包含钠或钾。

[0026] 在本发明的特别优选的实施方案中，获得了化学计量比的氮化镓GaN。

[0027] 优选地，根据本发明的方法在具有大于600cm^3、更优选大于9000cm^{3}的体积的高压釜中进行。

[0028] 本发明还包括通过以上方法获得的单晶含镓氮化物，其以至少0.1ppm的量包含第I族（IUPAC，1989）的至少一种元素，所述单晶含镓氮化物的特征在于，其以不高于1×10^{19}cm^{-3}、优选不高于3×10^{18}cm^{-3}、最优选不高于1×10^{18}cm^{-3}的浓度包含氧。

[0029] 在第一个优选实施方案中，本发明的氮化物是n型导电材料。

[0030] 在这种情况下，其以不高于1×10^{18}cm^{-3}、更优选不高于3×10^{17}cm^{-3}、最优选不高于1×10^{17}cm^{-3}的浓度包含选自镁、锌、镉或铍的受主，其中氧浓度相对于受主的总浓度的比不低于1.2。

[0031] 优选地，作为n型材料，本发明的氮化物显示出不高于7×10^{18}cm^{-3}、更优选不高于2×10^{18}cm^{-3}，最优选不高于7×10^{17}cm^{-3}的载流子（自由电子）浓度。

[0032] 在第二个优选实施方案中，本发明的氮化物是p型导电材料。

[0033] 在这种情况下，其以不高于2×10^{19}cm^{-3}、更优选不高于6×10^{18}cm^{-3}、最优选不高于2×10^{18}cm^{-3}的浓度包含选自镁、锌、镉或铍的受主，氧浓度相对于受主的总浓度的比不低于0.5。

[0034] 优选地，作为p型材料，本发明的氮化物显示出低于5×10^{17}cm^{-3}的载流子（自由空穴）的浓度。

[0035] 在第三个优选实施方案中，本发明的氮化物是高电阻(半绝缘)材料。

[0036] 在这种情况下，其以不高于$1\times10^{19}cm^{-3}$、更优选不高于$3\times10^{18}cm^{-3}$、最优选不高于$1\times10^{18}cm^{-3}$的浓度包含选自镁、锌、镉或铍的受主，其中氧浓度相对于受主的总浓度的比的范围为0.5至1.2。

[0037] 优选地，作为高电阻(半绝缘)材料，本发明的氮化物具有大于$1\times10^{5}\Omega\cdot cm$、更优选大于$1\times10^{6}\Omega\cdot cm$、最优选大于$1\times10^{9}\Omega\cdot cm$的电阻率。

[0038] 在本发明的特别优选的实施方案中，本发明的氮化物是化学计量比的氮化镓GaN。

[0039] 含镓氮化物是在其结构中至少具有镓原子和氮原子的化合物。含镓氮化物因此为至少二组分化合物GaN、三组分化合物AlGaN、InGaN以及四组分化合物AlInGaN，其优选以高于掺杂水平的水平包含大量的镓。在该化合物的结构中，其他元素相对于镓的组成可以在不干扰结晶技术中氨碱性的程度上变化。

[0040] 含镓原料是含镓氮化物或其前驱体。作为原料可以使用：金属镓，通过熔融法、HNP法、HVPE法获得的GaN，或者作为在超临界含氨溶剂中的反应的结果由金属镓获得的多晶GaN。

[0041] 矿化剂是在超临界含氨溶剂中提供一种或更多种碱金属离子，并且辅助原料(和含镓氮化物)的溶解的物质。

[0042] 超临界含氨溶剂是其中包含一种或更多种碱金属离子的至少由氨构成的超临界溶剂，所述离子辅助含镓氮化物的溶解。超临界含氨溶剂还可以包含氨的衍生物和/或它们的混合物，尤其是肼。

具体实施方式

[0043] 实施例1.获得经掺杂的GaN($Ca:NH_3=0.0005$，$Mg:NH_3=0.000005$，$Na:NH_3=0.04$)

[0044] 在体积为600cm³的高压釜中，在溶解区域中放置107.8g(约1.3mol)多晶GaN并添加有0.22g Ca(5.6mmol)及1.3mg Mg(0.05mmol)作为原料。还向高压釜引入10.34g(约449mmol)具有4N纯度的金属钠。

[0045] 使用通过HVPE法或通过从超临界含氨溶剂结晶而获得的18片单晶氮化镓作为晶种，单晶氮化镓垂直于单晶的c轴取向，直径为约25mm(1英寸)，各自的厚度为约500μm。将晶种放置在高压釜的结晶区域中。

[0046] 然后，以191g(约11.2mol)的量用氨(5N)填充高压釜，将其封闭并放入熔炉装置中。

[0047] 以约0.5℃/分钟的速度将溶解区域加热至450℃。此时，没有加热结晶区域。在溶解区域中到达450℃的预定温度后，即过程开始约15小时后，结晶区域中的温度为约170℃。在高压釜中使这个温度分布维持4天。此时，镓被部分携带至溶液，未溶解的镓完全转换成多晶GaN。然后，将结晶区域中的温度升高(以约0.1℃/分钟的速度)至550℃，而溶解区域中的温度保持不变。高压釜中的压力为约410MPa。这个温度分布的结果是在高压釜中区域之间出现对流，并且因此氮化镓从(上方)溶解区域化学运输至(下方)结晶区域，在结晶区域中沉积在晶种上。将获得的温度分布(即，溶解区域中为450℃，结晶区域为550℃)维持接下来的56天(至过程结束)。

[0048] 作为过程的结果，在溶解区域中原料(即，多晶GaN)部分溶解，并且在晶种上生长

(在每个晶种上)约1.75mm(在单晶的c轴方向上测量)的单晶氮化镓。由于该过程,获得了自由电子浓度为$4.8\times10^{18}cm^{-3}$、电阻率为$2\times10^{12}\Omega\cdot cm$的n型导电材料。通过二次离子质谱(SIMS)测量出的氧浓度为$9.0\times10^{18}cm^{-3}$,Mg的浓度为$9.5\times10^{16}cm^{-3}$。

[0049] 实施例2.获得经掺杂的GaN($Ca:NH_3=0.005,Mg:NH_3=0.000005,K:NH_3=0.08$)

[0050] 在体积为$9300cm^3$的高压釜中,在溶解区域中放置1.3kg(约16.3mol)多晶GaN并添加有37.6g Ca(940mmol)和23mg Mg(0.9mmol)作为原料。

[0051] 还向高压釜中引入了588g(约15mol)具有4N的纯度的金属钾。

[0052] 使用通过HVPE法或通过从超临界含氨溶剂结晶而获得的60片单晶氮化镓作为晶种,单晶氮化镓垂直于单晶的c轴取向,直径为约50mm(2英寸),各自的厚度为约1500μm。将晶种放置在高压釜的结晶区域中。

[0053] 然后,以3.2kg(约188mol)的量用氨(5N)填充高压釜,将其闭合并放入熔炉装置。

[0054] 加热(以约0.5℃/分钟的速度)溶解区域至550℃。此时,没有加热溶解区域。在溶解区域中到达450℃的预定温度后,即反应开始的约15小时后,结晶区域中的温度为约170℃。在高压釜中将这个温度分布维持4天。此时,镓被部分携带至溶液,未溶解的镓完全转换成多晶GaN。然后,将结晶区域中的温度升高(以约0.1℃/分钟的速度)至550℃,而溶解区域中的温度保持不变。高压釜中的压力为约410MPa。这个温度分布的结果是在高压釜中区域之间出现对流,并且因此氮化镓从(上方)溶解区域化学运输至(下方)结晶区域,在结晶区域中沉积在晶种上。将获得的温度分布(即,溶解区域中为450℃,结晶区域为550℃)维持接下来的56天(至过程结束)。

[0055] 作为过程的结果,获得了(在每个晶种上)厚度约为1.8mm(在单晶的c轴方向测量)的GaN层。获得了电阻率为$5\times10^{-2}\Omega\cdot cm$、自由电子浓度为$1.2\times10^{18}cm^{-3}$的n型导电的导电材料。通过二次离子质谱(SIMS)测量出的氧浓度为$9.4\times10^{17}cm^{-3}$,Mg的浓度为$9.0\times10^{16}cm^{-3}$。

[0056] 实施例3.获得经掺杂的GaN($Ca:NH_3=0.05,Mg:NH_3=0.000005,Na:NH_3=0.08$)

[0057] 除了使用1.1kg金属镓(16.3mol)、376g Ca(约9.4mol)、23mg Mg(0.9mmol)、345g Na(15mol)作为固体基质以外,进行与实施例2相同的步骤。

[0058] 作为过程的结果,获得了(在每个晶种上)厚度约为1.6mm(在单晶的c轴方向测量)的GaN层。获得了电阻率为$8\times10^{-2}\Omega\cdot cm$、电子浓度为$1.1\times10^{18}cm^{-3}$的导电n型材料。通过二次离子质谱(SIMS)测量出的氧浓度为$1.3\times10^{18}cm^{-3}$(饱和的氧水平与升高的Ca浓度),Mg的浓度为$5\times10^{16}cm^{-3}$。

[0059] 实施例4.获得经掺杂的GaN($Ca:NH_3=0.005,Mg:NH_3=0.00002,Na:NH_3=0.04$)

[0060] 除了使用89.8g金属镓(1.29mol)、2.25g Ca(约56.2mmol)、5.4mg Mg(约0.22mmol)、10.4g Na(0.45mol)作为固体基质以外,进行与实施例1相同的步骤。

[0061] 作为过程的结果,获得了(在每个晶种上)厚度约为1.73mm(在单晶的c轴方向测量)的GaN层。获得了电阻率$>10^6\Omega\cdot cm$的高电阻材料。通过二次离子质谱(SIMS)测量出的氧浓度为$8.2\times10^{17}cm^{-3}$,Mg的浓度为$1.1\times10^{18}cm^{-3}$。

[0062] 实施例5.获得经掺杂的GaN($Ca:NH_3=0.005,Mg:NH_3=0.00005,Na:NH_3=0.04$)

[0063] 除了使用89.8g金属镓(1.29mol)、2.25g Ca(约56.2mmol)、13mg Mg(约0.56mmol)、10.4g Na(0.45mol)作为固体基质以外,进行与实施例1相同的步骤。

[0064] 作为过程的结果，获得了(在每个晶种上)厚度约为1.79mm(在单晶的c轴方向测量)的GaN层。获得了载流子(自由空穴)的浓度为$3\times10^{16}cm^{-3}$、电阻率为$2\times10^{1}\Omega\cdot cm$的p型导电材料。通过二次离子质谱(SIMS)测量出的氧浓度为$1.3\times10^{18}cm^{-3}$，Mg的浓度为$5\times10^{18}cm^{-3}$。

[0065] 实施例6.获得经掺杂的GaN(Ca:NH_3＝0.005，Mg:NH_3＝0.0002，K:NH_3＝0.12)

[0066] 除了使用107.8g多晶GaN(1.3mol)、2.25g Ca(56.2mmol)、0.05g Mg(约2.25mmol)、52.7g K(1.3mol)作为固体基质以外，进行与实施例1相同的步骤。

[0067] 作为过程的结果，获得了(在每个晶种上)厚度约为1.7mm(在单晶的c轴方向测量)的GaN层。获得了载流子(自由空穴)的浓度为$1.8\times10^{17}cm^{-3}$，电阻率为$7\times10^{1}\Omega\cdot cm$的p型导电材料。

[0068] 通过二次离子质谱(SIMS)测量出的氧浓度为$1.5\times10^{18}cm^{-3}$，Mg的浓度为$8\times10^{18}cm^{-3}$。

[0069] 实施例7.获得经掺杂的GaN(Gd:NH_3＝0.001，Mg:NH_3＝0.000005，Na:NH_3＝0.04)

[0070] 除了使用89.8g金属镓(1.3mol)、1.8g Gd(11.2mmol)、1.3mg Mg(约0.056mmol)、10.3g Na(0.45mol)作为固体基质以外，进行与实施例1相同的步骤。

[0071] 作为过程的结果，获得了(在每个晶种上)厚度约为1.9mm(在单晶的c轴方向测量)的GaN层。获得了自由电子的浓度为$2\times10^{17}cm^{-3}$、电阻率为$6\times10^{-2}\Omega\cdot cm$的n型导电材料。通过二次离子质谱(SIMS)测量出的氧浓度为$1.2\times10^{18}cm^{-3}$，Mg的浓度为$5\times10^{17}cm^{-3}$。

[0072] 实施例8.获得经掺杂的GaN(Gd:NH_3＝0.001，Mg:NH_3＝0.00002，K:NH_3＝0.08)

[0073] 除了使用107.8g多晶GaN(1.3mol)、1.8g Gd(11.2mmol)、5mg Mg(约0.22mmol)、35.2g K(0.9mol)作为固体基质以外，进行与实施例1相同的步骤。

[0074] 作为过程的结果，获得了(在每个晶种上)厚度约为1.6mm(在单晶的c轴方向测量)的GaN层。获得了电阻率$>1\times10^{6}\Omega\cdot cm$的高电阻材料。通过二次离子质谱(SIMS)测量出的氧浓度为$8\times10^{17}cm^{-3}$，Mg的浓度为$1.2\times10^{18}cm^{-3}$。

[0075] 实施例9.获得经掺杂的GaN(Gd:NH_3＝0.0075；Ca:NH_3＝0.0025；Mg:NH_3＝0.00015；Zn:NH_3＝0.00005；K:NH_3＝0.12)

[0076] 除了使用107.8g多晶GaN(1.3mol)、13.2g Gd(84.3mmol)、1.1g Ca(28.1mmol)、41mg Mg(约1.7mmol)、36mg Zn(0.56mmol)以及52.7g K(1.35mol)作为固体基质以外，进行与实施例1相同的步骤。

[0077] 作为过程的结果，获得了(在每个晶种上)厚度约为1.65mm(在单晶的c轴方向测量)的GaN层。获得了电阻率为$1.5\times10^{1}\Omega\cdot cm$，载流子(自由空穴)的浓度为$7\times10^{16}cm^{-3}$的p型材料。通过二次离子质谱(SIMS)测量出的氧的浓度为$9\times10^{17}cm^{-3}$，Mg的浓度为$4.5\times10^{18}cm^{-3}$，Zn的浓度为$1.5\times10^{18}cm^{-3}$。

[0078] 实施例10.获得经掺杂的GaN(Gd:NH_3＝0.001，Zn:NH_3＝0.000005，Na:NH_3＝0.04)

[0079] 除了使用1.1kg金属镓(16.3mol)、29.5g Gd(188mmol)、61mg Zn(约0.9mmol)以及173g Na(7.5mol)作为固体基质以外，进行与实施例2相同的步骤。

[0080] 作为过程的结果，获得了(在每个晶种上)厚度约为1.72mm(在单晶的c轴方向测量)的GaN层。获得了自由电子的浓度为$6\times10^{17}cm^{-3}$，电阻率为$3\times10^{-2}\Omega\cdot cm$的n型材料。通过二次离子质谱(SIMS)测量的氧的浓度为$1.1\times10^{18}cm^{-3}$，Zn的浓度为$1.2\times10^{17}cm^{-3}$。

[0081] 实施例11.获得经掺杂的GaN(Gd:NH_3＝0.0075,Y:NH_3＝0.0025,Zn:NH_3＝0.00002,K:NH_3＝0.04)

[0082] 除了使用107.8g多晶GaN(1.3mol)、13.2g Gd(约84.3mmol)、2.5g Y(约28.1mmol)、14mg Zn(0.22mmol)以及17.6g K(0.45mmol)作为固体基质以外,进行与实施例1相同的步骤。

[0083] 作为过程的结果,获得了(在每个晶种上)厚度约为1.8mm(在单晶的c轴方向测量)的GaN层。获得了自由电子的浓度为$1\times10^{17}cm^{-3}$、电阻率为$8\times10^{-2}\Omega\cdot cm$的n型材料。通过二次离子质谱(SIMS)测量出的氧的浓度为$9\times10^{17}cm^{-3}$,Zn的浓度为$6\times10^{17}cm^{-3}$。

[0084] 实施例12.获得经掺杂的GaN(Gd:NH_3＝0.001,Zn:NH_3＝0.00005,Na:NH_3＝0.08)

[0085] 除了使用89.8g金属镓(1.3mol)、1.8g Gd(11.2mmol)、36mg Zn(约0.5mmol)以及20.6g Na(0.9mol)作为固体基质以外,进行与实施例1相同的步骤。

[0086] 作为过程的结果,获得了(在每个晶种上)厚度约为1.76mm(在单晶的c轴方向测量)的GaN层。获得了电阻率＞$10^6\Omega\cdot cm$的高电阻材料。通过二次离子质谱(SIMS)测量出的氧的浓度为$9.8\times10^{17}cm^{-3}$,Zn的浓度为$1.2\times10^{18}cm^{-3}$。

[0087] 实施例13.获得经掺杂的GaN(Gd:NH_3＝0.001,Zn:NH_3＝0.0002,Na:NH_3＝0.08)

[0088] 除了使用107.8g多晶GaN(1.3mol)、1.8g Gd(11.2mmol)、0.14g Zn(约2.2mmol)以及20.6g Na(0.9mol)作为固体基质以外,进行与实施例1相同的步骤。

[0089] 作为过程的结果,获得了(在每个晶种上)厚度约为1.68mm(在单晶的c轴方向测量)的GaN层。获得了自由载流子(空穴)的浓度为$1\times10^{16}cm^{-3}$,电阻率为$2\times10^{2}\Omega\cdot cm$的p型材料。通过二次离子质谱(SIMS)测量出的氧的浓度为$8.2\times10^{17}cm^{-3}$,Zn的浓度为$4.2\times10^{18}cm^{-3}$。

[0090] 实施例14.获得经掺杂的GaN(Y:NH_3＝0.01,Zn:NH_3＝0.000005,K:NH_3＝0.04)

[0091] 除了使用1.1kg金属镓(16.3mol)、167g钇(Y)(1.9mol)、60mg Zn(0.9mmol)以及294g K(7.5mol)作为固体基质以外,进行与实施例2相同的步骤。

[0092] 作为过程的结果,获得了(在每个晶种上)厚度约为1.8mm(在单晶的c轴方向测量)的GaN层。获得了自由载流子(电子)的浓度为$2.3\times10^{18}cm^{-3}$、电阻率为$8\times10^{-2}\Omega\cdot cm$的n型材料。

[0093] 通过二次离子质谱(SIMS)测量出的氧的浓度为$3\times10^{18}cm^{-3}$,Zn的浓度为$2.1\times10^{17}cm^{-3}$。

[0094] 实施例15.获得经掺杂的GaN(Y:NH_3＝0.01,Zn:NH_3＝0.00005,Na:NH_3＝0.08)

[0095] 除了使用89.8g金属镓(1.3mol)、10g钇(Y)(112mmol)、36mg Zn(0.56mmol)、20.7g Na(0.9mol)作为固体基质以外,进行与实施例1相同的步骤。

[0096] 作为过程的结果,获得了(在每个晶种上)厚度为约1.7mm(在单晶的c轴方向测量)的GaN层。获得了电阻率＞$10^6\Omega\cdot cm$的高电阻材料。通过二次离子质谱(SIMS)测量出的氧的浓度为$3.2\times10^{18}cm^{-3}$,Zn的浓度为$4\times10^{18}cm^{-3}$。

[0097] 实施例16.获得经掺杂的GaN(Y:NH_3＝0.01,Zn:NH_3＝0.00015,Mg:NH_3＝0.00005,K:NH_3＝0.12)

[0098] 除了使用89.8g金属镓(1.3mol)、10g钇(Y)(112mmol)、0.11g Zn(1.7mmol)、14mg Mg(0.56mmol)、52.7g K作为固体基质以外,进行与实施例1相同的步骤。

[0099] 作为过程的结果，获得了(在每个晶种上)厚度约为1.75mm(在单晶的c轴方向测量)的GaN层。获得了自由载流子(空穴)的浓度为$2\times10^{16}cm^{-3}$，电阻率为$3\times10^{1}\Omega\cdot cm$的p型材料。通过二次离子质谱(SIMS)测量出的氧的浓度为$2.5\times10^{18}cm^{-3}$，Zn的浓度为$5.7\times10^{18}cm^{-3}$，Mg的浓度为$1.8\times10^{18}cm^{-3}$。