

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 November 2007 (01.11.2007)

PCT

(10) International Publication Number
WO 2007/123735 A1

(51) International Patent Classification:
C30B 29/40 (2006.01) **C30B 33/00** (2006.01)
C30B 23/00 (2006.01)

(21) International Application Number:
PCT/US2007/007980

(22) International Filing Date: 30 March 2007 (30.03.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/787,399 30 March 2006 (30.03.2006) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, 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, 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, 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, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, 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
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHODS FOR CONTROLLABLE DOPING OF ALUMINUM NITRIDE BULK CRYSTALS

(57) Abstract: Fabrication of doped and undoped stoichiometric polycrystalline AlN ceramics with high purity is accomplished by, for example, reacting Al pellets with nitrogen gas. Such polycrystalline AlN ceramics may be utilized in the fabrication of high purity AlN single crystals, which may be annealed to enhance a conductivity thereof.



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METHODS FOR CONTROLLABLE DOPING OF ALUMINUM NITRIDE BULK CRYSTALS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims the benefits of and priority to U.S. Provisional Application Serial No. 60/787,399, filed on March 30, 2006, the entire disclosure of which is hereby incorporated by reference.

GOVERNMENT SUPPORT

5 [0002] This invention was made with United States Government support under 70NANB4H3051 awarded by the National Institute of Standards and Technology (NIST). The United States Government has certain rights in the invention.

BACKGROUND

10 [0003] Semiconductor materials exhibit controllable optical and electrical properties, such as conductivity, over a wide range. Such control is enabled by use of dopants, which are impurities introduced into the crystalline lattice of the semiconductor material to serve as sources of electrons (negative charges) or holes (positive charges). Controllable doping enables the fabrication of a wide range of semiconductor devices, e.g., light-emitting diodes (LEDs), lasers, and transistors.

15 [0004] Nitride-based semiconductors such as gallium nitride (GaN) and aluminum nitride (AlN) are of great interest technologically, in part because of their wide bandgaps. Controllable and repeatable doping of these materials enables the fabrication of light-emitting devices, such as LEDs and lasers, that emit light at short wavelengths, i.e., at blue, violet, and even ultraviolet wavelengths. Moreover, n- and p-type nitrides can be utilized in the fabrication
20 of transistors suited for high power and/or high temperature applications. In an n-type semiconductor, the concentration of electrons is much higher than the concentration of holes; accordingly, electrons are majority carriers and dominate conductivity. In a p-type semiconductor, by contrast, holes dominate conductivity.

[0005] AlN has a relatively large bandgap of 6.1 electron volts (eV) at room
25 temperature, and few dopants for AlN have shallow enough energy levels in the bandgap to facilitate high electrical conductivity with only moderate impurity (i.e., dopant) concentrations.

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Thus, impurity concentrations often need to be relatively high in order to achieve technologically useful conductivity levels. Unfortunately, achieving high impurity concentration levels in AlN can be difficult. AlN is typically grown at very high temperatures, making it difficult to incorporate high levels of desired dopants in a controlled way while
5 avoiding the introduction of unwanted impurities and other point defects. These will introduce deep levels in the bandgap that counteract the desired effect of the dopant. (That is, the undesired defects will introduce deep levels that will absorb the electrons or holes introduced by the dopant impurities.) In particular, under typical growth conditions, oxygen appears to introduce a deep level in the AlN bandgap and needs to be carefully controlled if conducting
10 crystals are to be produced. Thus, success in creating large, conductive crystals has proven elusive even though AlN thin films with n-type conductivity have been demonstrated.

DESCRIPTION OF THE INVENTION

Brief Summary of the Invention

[0006] In accordance with the present invention, a donor or acceptor level is created
15 within the perfect, stoichiometric AlN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (where $0 \leq x \leq 1$, herein sometimes referred to as AlGa_N) lattice by introducing a substitutional impurity that has greater or fewer electrons than aluminum (Al) or nitrogen (N). Charge-compensating defects, such as vacancies on the Al cation site (designated as V_{Al}) or the N anion site (designated as V_{N}) or impurities with deep levels which will trap the free charge created by the doping impurity, are desirably
20 avoided but, more generally, are either reduced in density or less active. In order to use atoms that have nearly the same diameter as Al or N and avoid local strain, dopants are preferably selected from the upper part of the periodic table. Choices for the Al site include beryllium (Be), magnesium (Mg), zinc (Zn), carbon (C), and silicon (Si) while C, Si, and oxygen (O) are possible choices for the N site. Dopants with two fewer electrons than Al, such as lithium (Li),
25 may also be used to make p-type AlN and AlGa_N if they can be introduced on the Al site.

[0007] Unfortunately, as explained above, creating donor or acceptor levels with dopants is generally difficult in a material like AlN. The energy levels from most dopants in AlN will tend to be rather deep in the energy bandgap, making it difficult to achieve reasonable conductivity levels unless high concentrations of the dopant are used. In addition, the wide-
30 bandgap AlN crystal has a tendency to form charge-compensating vacancy defects such as V_{Al} or V_{N} .

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[0008] Accordingly, in a first aspect, the invention features a method of forming polycrystalline AlN. In various embodiments, an Al-containing pellet is provided in a crucible and the pellet is reacted at a reaction temperature and a reaction pressure with nitrogen gas to form a polycrystalline AlN ceramic that is approximately stoichiometric. The pellet may consist essentially of Al, and the reaction temperature may be within the range of approximately 1900 °C to approximately 2200 °C. The pellet may include a first concentration, which may be less than approximately 12% by weight, of a dopant species, which may be Si. In an embodiment, the polycrystalline AlN ceramic includes a second concentration of the dopant species. The second concentration may be less than approximately 12% by weight. The reaction temperature may be within the range of approximately 1600 °C to approximately 2200 °C, and the reaction pressure may be within the range of approximately 1 bar to approximately 60 bars.

[0009] Embodiments of the invention may include one or more of the following features. An oxygen concentration of the polycrystalline AlN ceramic may be less than approximately 400 parts per million (ppm), or less than 100 ppm. Substantially all of the pellet may be reacted to form the polycrystalline AlN ceramic. At least one additional Al-containing pellet may be provided within the crucible and reacted at the reaction temperature and the reaction pressure with nitrogen gas in order to increase the volume of the polycrystalline AlN ceramic.

[0010] In an embodiment, the polycrystalline AlN ceramic is provided at the first end of and within a crystal growth enclosure and sublimed at a formation temperature, forming an AlN single crystal at the second end of the crystal growth enclosure. The formation temperature may be within the range of approximately 2000°C to approximately 2750 °C. The oxygen concentration of the AlN single crystal may be less than approximately 400 ppm, less than approximately 100 ppm, or less than approximately $4.5 \times 10^{19} / \text{cm}^3$. The thermal conductivity of the AlN single crystal may be greater than approximately 250 Watts per meter-Kelvin (W/m·K). The polycrystalline AlN ceramic may include a dopant species, which may be present within the AlN single crystal at a first concentration. The dopant species may be Si, and the first concentration may be greater than approximately $10^{16} / \text{cm}^3$. The AlN single crystal may have a conductivity greater than approximately $10^{-4} \Omega^{-1} \text{cm}^{-1}$ at room temperature. At least a portion of the crucible may be proximate and in contact with the polycrystalline AlN ceramic during formation of the AlN single crystal.

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[0011] In a second aspect, the invention features a method of forming a doped AlN wafer. In various embodiments, a single-crystal wafer including AlN and a dopant species is provided and the wafer is annealed to electrically activate the dopant species. The dopant species may include Si. Annealing may decrease the concentration of aluminum vacancies, or
5 increase the concentration of nitrogen vacancies, in the single-crystal wafer. In an embodiment, the step of annealing is performed at an annealing temperature and an annealing nitrogen pressure, and the annealing nitrogen pressure is greater than approximately a nitrogen pressure required to form AlN from aluminum at the annealing temperature. The annealing nitrogen pressure may be less than approximately twice the nitrogen pressure required to form AlN from
10 aluminum at the annealing temperature, or may be within the range of approximately 0.1 millibar (mbar) to approximately 5 bars. The annealing temperature may be greater than approximately 1900 °C. After annealing, the single-crystal wafer may have a conductivity at room temperature greater than approximately $10^{-4} \Omega^{-1}\text{cm}^{-1}$, or greater than approximately $10^{-2} \Omega^{-1}\text{cm}^{-1}$.

[0012] In a third aspect, the invention features a method of forming an AlN wafer. In various embodiments, a single-crystal wafer including undoped AlN and having a first conductivity is provided, and the single-crystal wafer is annealed in an ambient at an annealing temperature and an annealing pressure, where after annealing the single-crystal wafer has a second conductivity greater than the first conductivity. The annealing temperature may be
20 within a range of approximately 1700 °C to approximately 2200 °C, and the annealing pressure may be within a range of approximately 2 bars to approximately 30 bars. The ambient may consist essentially of nitrogen and at least one inert gas, which may be argon. The pressure of nitrogen in the ambient may be greater than a nitrogen pressure required to form AlN from aluminum at the first temperature. The second conductivity may be greater than approximately
25 $10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature.

[0013] In yet another aspect, the invention features an AlN single crystal having a thickness greater than approximately 100 micrometers (μm), a cross-sectional area greater than approximately 1 cm^2 , and a conductivity greater than approximately $10^{-4} \Omega^{-1}\text{cm}^{-1}$ at room temperature. The AlN single crystal may include a substitutional dopant species, and may
30 exhibit n-type conductivity. The substitutional dopant species may include a group IV element, which may be Si. The AlN single crystal may consist essentially of AlN and nitrogen vacancies. The thickness may be greater than approximately 200 μm , or even greater than

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approximately 2 millimeters (mm). The conductivity may be greater than approximately $10^{-2} \Omega^{-1} \text{cm}^{-1}$ at room temperature, and a thermal conductivity of the AlN single crystal may be greater than approximately 250 W/m·K.

Brief Description of the Drawings

- 5 **[0014]** In the drawings, like reference characters generally refer to the same parts throughout the different views. Also, the drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the present invention are described with reference to the following drawings, in which:
- 10 **[0015]** Fig. 1 schematically depicts a crystal growth enclosure for the growth of single-crystalline AlN;
- [0016]** Figs. 2A and 2B are schematic diagrams of a furnace utilized for the formation of polycrystalline source material as described in one embodiment of the invention;
- [0017]** Figs. 3A-3E are schematic diagrams of a reactor utilized for the formation of polycrystalline source material as described in another embodiment of the invention; and
- 15 **[0018]** Fig. 4 schematically depicts an AlN wafer separated from a boule of single-crystalline AlN.

Detailed Description of the Preferred Embodiments

- 20 **[0019]** A representative environment for practice of embodiments of the present invention is shown in Fig. 1. AlN crystals can be formed by the sublimation-recondensation method described in U.S. Patent Application Serial No. 11/503,660, the entire disclosure of which is herein incorporated by reference. A crystal growth enclosure 100 includes a vapor mixture 110, an AlN crystal 120, and a polycrystalline source 130, and is surrounded by a furnace 140. In an embodiment, crystal growth enclosure 100 includes tungsten. In alternative
- 25 embodiments, crystal growth enclosure 100 includes a tungsten-rhenium alloy, rhenium, carbon, tantalum carbide, tantalum nitride, tantalum carbo-nitride, hafnium nitride, mixtures of tungsten and tantalum, or a combination thereof, as described in U.S. Patent Application Serial No. 10/822,336, the entire disclosure of which is hereby incorporated by reference.
- 30 **[0020]** Vapor mixture 110 arises from the heating of polycrystalline source 130 at one end of crystal growth enclosure 100, and coalesces into AlN crystal 120 at another, cooler end. Polycrystalline source 130 may be a ceramic material, may comprise or consist essentially of

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AlN, and may further include at least one interstitial or substitutional dopant. AlN crystal 120 may be single crystal, and may include finite concentrations of interstitial or substitutional dopants. Upon further treatment, the dopants can be electrically activated to dope AlN crystal 120 and provide it with desirable electrical properties. In all embodiments described herein, AlN crystal 120 may also include gallium (Ga), rendering it an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ crystal. For example, Ga may be added to polycrystalline source 130 such that the crystal coalesces as $\text{Al}_x\text{Ga}_{1-x}\text{N}$. In such a case, the crystal may have an Al concentration greater than approximately 50%. AlN crystal 120 may have a thickness of greater than approximately 0.1 mm and a diameter greater than approximately 1 cm. The diameter may even be greater than approximately 2 cm. AlN crystal 120 may be single crystalline.

[0021] The ensuing discussion describes selection of dopant species for AlN crystal 120 (and therefore for polycrystalline source 130), as well as techniques for producing various types of polycrystalline source 130 with desired properties (e.g., dopant and purity concentrations), before returning to the details of fabricating AlN crystal 120 and subsequent processing thereof.

Dopant Selection

[0022] In accordance with the present invention, the first step in making doped AlN crystal 120 is identifying which impurities or impurity pairs may produce donor or acceptor centers with a small activation energy. For the Al site, appropriate single-element donors may be Group IV elements such as Si, Ge, and/or transition elements such as Ti, V, etc., while for the N site, Group VI elements such as O and/or S may be used as donors. If interstitial sites are considered, lighter elements, such as H or Li, may be suitable donors. If one considers co-doping with molecular impurities where both donors and acceptors are incorporated on the same sublattice, then impurities such as BeSiN_2 , ZnSiN_2 , MgSiN_2 , LiSi_2N_3 , and Al_2OC may be considered, as described in U.S. Patent Application Serial No. 11/633,667, the entire disclosure of which is hereby incorporated by reference. All of these approaches desirably require the controlled introduction of impurities into the crystal during the bulk crystal growth process. Two other possible dopant-generation schemes are nuclear-transmutation doping and in-diffusion of the dopant from the crystal surface. However, these last two approaches may be more difficult with bulk crystals thicker than approximately 2 mm because diffusion times may be too long to be practical and the implantation energies required may be too high. Hence, the present invention preferably utilizes dopants that may be introduced during bulk crystal growth.

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[0023] The next step is to select an appropriate dopant, i.e., one that can withstand the sublimation-recondensation growth process at temperatures up to 2330 °C (at which temperature tungsten crucibles may undergo a eutectic reaction) or hotter if an alternative crucible is used. (U.S. Patent No. 6,719,843, the entire disclosure of which is hereby
5 incorporated by reference, describes other possible crucible materials for growth of AlN bulk single crystals.) In AlN and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ thin epitaxial films, it has been found that Si is a shallow donor. In Si-doped GaN, n-type carrier concentrations at room temperature up to $1 \times 10^{20} / \text{cm}^3$ have been achieved. It has been observed to become degenerate above about $1 \times 10^{18} / \text{cm}^3$ of Si, i.e., the conductivity is observed to become temperature-independent due to the
10 high density of dopant. In Si-doped AlN, the highest room-temperature carrier concentration obtained appears to be about $2 \times 10^{20} / \text{cm}^3$. The following discussion addresses the factors limiting Si solubility in AlN and its electrical activation, as well as the implications for crystal growth.

[0024] The covalent radii of Al and Si are quite similar. In AlN, the average Al-N bond
15 distance is 1.89 Å. Thus, Si atoms are about 10% smaller than Al atoms in these nitrides. In the pseudobinary system AlN-Si₃N₄ one ternary compound, Si₃Al₅N₉, is known. It may only exist in the presence of oxygen as an impurity. While the solid solubility limit of Si₃N₄ in AlN (or of AlN in Si₃N₄) at room temperature or at higher temperatures is somewhat uncertain (and is discussed below), there is ample evidence to show that concentrations attractive to doping
20 AlN are possible and are stable at the temperatures required for bulk crystal growth of AlN.

[0025] It has been shown that Si-doped AlN exhibits excellent blue luminescence, both photoluminescence and cathodoluminescence. This result has encouraged several studies of the upper limit of r , defined to be the Si/Al atom ratio in Si-doped AlN. In analogy with typical solubility behavior, we expect that as the temperature increases, the solubility of Si₃N₄ in AlN
25 will increase.

Formation of AlN ceramic with controlled impurity concentrations

[0026] Providing a polycrystalline source 130 that includes AlN with carefully controlled impurity concentrations (including the elimination of potential deep-level impurities such as oxygen) enables growth of AlN with controllable electrical and optical properties.
30 Generally, oxygen is a common contaminant, and the highest-purity AlN material that can be purchased commercially has oxygen impurities at a level exceeding 0.3% by weight (3,000

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ppm by weight). Because the vapor pressures of oxides of aluminum are much higher than those of Al or of N₂ above contaminated AlN, the commercial powder may be purified by heating to 2,000 °C or so in a clean N₂ atmosphere. Unfortunately, the contaminated powder will tend to sinter during the heating cycle and become dense while trapping the residual oxygen within the sintered mass. An alternative approach is to sublime (i.e., congruently evaporate Al and N₂ molecules) the contaminated AlN in a N₂ atmosphere under a temperature gradient so that AlN will recondense at a colder place in the furnace. Aluminum oxynitrides will condense at even colder temperatures and so higher purity AlN ceramic will be physically separated from the aluminum oxynitride. While this process is useful in obtaining higher-purity AlN, it is time consuming and requires the dedication of a high temperature furnace since reasonable evaporation rates will require the furnace to be operated at temperatures above 2200 °C. In addition, it is difficult to obtain AlN with oxygen impurity concentrations below 400 ppm with this method, probably due to the solubility of oxygen in the AlN crystal.

[0027] Herein, oxygen concentrations are preferably measured by the TCH600 Oxygen Determinator, available from LECO Corporation of St. Joseph, Michigan, the Neutron Activation Analysis technique, or by dynamic Secondary Ion Mass Spectroscopy (SIMS). The commercially available LECO measurement is reliable to at least a detection limit of 200 ppm by weight with normal non-inert atmosphere sample handling (surface contamination) of the oxygen-sensitive AlN. In addition, we have found neutron activation to be capable of a detection limit down to at least 100 ppm for polycrystalline ceramic material. For single crystal samples, accurate oxygen measurements may be made with dynamic SIMS which can be calibrated using isotope implant techniques to confirm the validity of the measurement. All of these measurement techniques are preferred over glow-discharge mass spectroscopy (GDMS), which is notoriously difficult and may give erroneously low measurements.

[0028] A more efficient way to make AlN with controllable impurities is to react, in high-purity nitrogen, either high-purity Al metal or Al metal that is doped with the impurity desired and nothing else. In Slack and McNelly, J. Crystal Growth 34, 263 (1976), the entire disclosure of which is hereby incorporated by reference, the problem of trying to burn Al directly in nitrogen is described. In particular, at atmospheric pressure, the Al will react to form a protective skin around the unreacted Al metal and the reaction will stop. It has been demonstrated (M. Bockowski, A. Witek, S. Krukowski, M. Wroblewski, S. Porowski, R.M. Ayral-Marin, and J.C. Tedenac, Journal of Materials Synthesis and Processing, 5, 449 (1997),

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the entire disclosure of which is hereby incorporated by reference) that very high nitrogen pressures can be used to keep the reaction going. However, the reacted AlN will form a powder and will quickly become contaminated when exposed to air. It is much more desirable to form a dense AlN material with limited surface area which will make it much easier to handle the AlN product without contaminating it.

[0029] In previous pellet-drop work by Slack and McNelly (J. Crystal Growth 42, 560 (1977), the entire disclosure of which is hereby incorporated by reference), Al pellets were dropped into a pyrolytic boron nitride (pBN) crucible that is heated to about 1850 °C in an RF-heated furnace. The individual pellets of Al were rapidly reacted to form relatively high purity AlN. Slack and McNelly obtained AlN with about 1% excess Al by weight and a residual oxygen contamination of about 400 ppm. After the AlN was formed, the pBN crucible had to be mechanically removed and the resulting AlN had to be sublimed in a temperature gradient in a nitrogen atmosphere. Slack and McNelly used the last step (sublimation and recondensation of the AlN polycrystalline material) to reduce the excess Al to less than 0.1%. This sublimation and recondensation step was reported to take between 12 and 24 hours for 70 grams of AlN product. In accordance herewith, a pellet-drop method produces AlN polycrystalline material with controlled dopant concentrations (including no dopants so that the AlN is high-purity) that can be used directly for AlN crystal growth without the extra step of subliming and recondensing the resulting AlN polycrystalline material. In addition, the resulting AlN polycrystalline material has lower oxygen contamination. Embodiments of the invention preferably utilize a crucible material that 1) does not react with the AlN polycrystalline material, and 2) may remain on the AlN polycrystalline material during subsequent sublimation-recondensation growth of AlN single crystals from the polycrystalline material.

[0030] Highly silicon-doped AlN can be produced by burning an Al-Si alloy in a nitrogen atmosphere at about 1850°C and at 1 bar or higher pressure. At 1875°C, the N₂ dissociation pressure of Si₃N₄ is approximately 1 bar, which may set a preferred upper limit on the burning temperature at 1 bar since Si₃N₄ formation may result at high Si concentrations. In this way, some or all of the Si becomes entrapped in the AlN lattice.

[0031] The Al-Si phase diagram shows that the maximum equilibrium solid solubility of Si in metallic Al is 1.59 atom% at 577°C. If the liquid alloys are rapidly quenched, then considerably more Si can be trapped in solid solution in the Al metal. In fact, high-purity Si-doped Al can be purchased with Si concentrations of up to 3.5%, although it is likely that

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higher concentrations of Si in Al may be obtained through rapid quenching of a molten Al and Si mixture.

[0032] Below two examples are given of forming polycrystalline AlN material with controlled dopant concentrations.

5 **Production of doped, high-density AlN polycrystalline material**

[0033] Referring to Figs. 2A and 2B, a furnace 200 is utilized in the formation of polycrystalline source 130 incorporating a high concentration of at least one substitutional dopant. Furnace 200 includes a pellet loading mechanism 210, which drops pellets comprising or consisting essentially of Al into a crucible 220. In an embodiment, the pellets may be doped
10 with one or more dopant species. In an embodiment, the dopant concentration in the pellets is less than 12% by weight. Crucible 220 includes a bottom plug 230 and a foil wrap 240. Bottom plug 230 may be approximately cylindrical with, e.g., a diameter of approximately 0.625 inches and a height of approximately 0.5 inches. Bottom plug 230 may comprise or consist essentially of tungsten (W), or another high-melting-point material inert to AlN. Foil
15 wrap 240 wraps around bottom plug 230, forming a cylinder open at the top and sealed at the bottom by bottom plug 230. Foil wrap 240 may comprise or consist essentially of W, or another high-melting-point material inert to AlN, and may have a thickness of approximately 0.001 inch. In an embodiment, foil wrap 240 may be wrapped around bottom plug 230 multiple times, e.g., a three-ply foil wrap 240 is formed by wrapping W foil around bottom plug
20 230 three times. Foil wrap 240 is held in place by at least one wire 250, which may comprise or consist essentially of a tungsten-rhenium alloy (e.g., 25% rhenium) and have a thickness of approximately 0.01 inch.

[0034] Crucible 220 is disposed within a susceptor 260 and on top of a crucible stand 270. Both susceptor 260 and crucible stand 270 may comprise or consist essentially of W. A
25 crucible funnel 280 is disposed above the top opening of crucible 220, and may comprise or consist essentially of molybdenum (Mo). Crucible funnel 280 is shaped to direct pellets from pellet loading mechanism 210 into crucible 220.

[0035] Furnace 200 is resistively heated by one or more heating elements 290, which are surrounded by insulation 292. Heating elements 290 may be heated to temperatures up to
30 approximately 2300 °C, and furnace 200 may operate at pressures up to approximately 60 bar. In an exemplary embodiment, the furnace operates at pressures up to approximately 10 bar.

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Generally, elevated pressures may enable the incorporation of high concentrations of dopants into polycrystalline source 130 (as described below) by limiting evaporation of the dopant species or a compound thereof. For example, when Si is utilized as a dopant, high furnace pressures may substantially prevent the evaporation of the Si in the form of Si_3N_4 . Gas flows into furnace 200 from a bottom inlet 294 and is exhausted through a top outlet 296. The gas may comprise or consist essentially of nitrogen or a mixture of nitrogen and 3% hydrogen (i.e., forming gas), and is filtered by a gas filter (not shown) that reduces levels of contaminants such as oxygen, water vapor, and hydrocarbons to less than 10 parts per billion (ppb). An upper funnel 298 connects pellet loading mechanism 210 to crucible funnel 280.

[0036] In order to form doped polycrystalline source 130, pellets are desirably cleaned in preparation for loading into pellet loading mechanism 210. The pellets are preferably all similarly sized and shaped to facilitate automatic handling (as described below). First, the pellets are sifted in order to remove oddly shaped pellets or small shavings. The pellets are then ultrasonically cleaned in distilled water for approximately 20 minutes. Next, the pellets are immersed in a mixture of hydrofluoric acid (HF) and nitric acid (HNO_3) for approximately 2 minutes at room temperature. Finally, the pellets are rinsed in distilled water and multiple times in methanol, whereupon they may be stored in an inert atmosphere prior to loading into pellet loading mechanism 210. Cleaning doped or undoped Al pellets is important to produce consistent results and to provide a consistent surface oxidation (or reduced layer thereof) to the reaction for production of both doped and undoped polycrystalline source 130.

[0037] Crucible 220 is loaded into furnace 200, and the pellets are loaded into pellet loading mechanism 210. A cleaning cycle, in which the pellets are not dropped into crucible 220, may be run prior to an actual reaction cycle in which polycrystalline source 130 is formed. Furnace 200 is alternately subjected to a flow of forming gas and evacuated several times (e.g., three times). Heating elements 290 are heated to approximately 2200 °C, thus heating crucible 220 to approximately 1950 °C. Forming gas is flowed through furnace 200 at a high rate, e.g., approximately 0.25 liters per minute (lpm) in order to purge residual moisture and to reduce any W-containing components therein (which may have oxidized due to exposure to air or other sources of contamination). Heating elements 290 are then cooled back down to room temperature.

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[0038] A reaction cycle is then performed to form polycrystalline source 130. Furnace 200 is alternately subjected to a flow of nitrogen and evacuated several times (e.g., three times). The reaction cycle may be performed at temperatures within the range of approximately 1600 °C to approximately 2200 °C, and at pressures within the range of approximately 1 bar to approximately 60 bars. In an embodiment, the reaction cycle is performed at a pressure less than approximately 10 bar. In an exemplary embodiment, under a nitrogen pressure of approximately 1.5 bars and a nitrogen flow of approximately 0.25 lpm, heating elements 290 are heated to approximately 1800 °C (corresponding to a temperature of crucible 220 of approximately 1650 °C) and held at that temperature for approximately three hours. The gas flow is decreased to approximately 5 standard cubic centimeters per minute (sccm), and the pellets are dropped from pellet loading mechanism 210, through upper funnel 298 and crucible funnel 280, into crucible 220. The pellets may each weigh approximately 72 milligrams, and may be dropped at a rate of approximately 1 per minute. The pellets land on bottom plug 230 (or the portion of polycrystalline source 130 already produced thereon), melt, and react with the nitrogen gas to form polycrystalline source 130. Dopants present in the pellets are incorporated into polycrystalline source 130 at concentrations at least partially determined by the dopant concentration in the pellets and by the reaction kinetics. Very high dopant concentrations in polycrystalline source 130, e.g., up to approximately 12% by weight, may be achieved by using very high concentrations of dopant in the pellet and by suppressing dopant evaporation by increasing the nitrogen pressure in reaction furnace 200. Each subsequent pellet dropped from pellet loading mechanism 210 reacts and increases the size and volume of polycrystalline source 130. In an embodiment, substantially all of each pellet reacts to form polycrystalline source 130.

[0039] After the reaction cycle, furnace 200 (and polycrystalline source 130) is cooled down to approximately room temperature over approximately 1 hour at a positive nitrogen pressure. Thus formed, polycrystalline source 130 may weigh up to approximately 80 grams, and may include low concentrations of impurities such as oxygen, boron, and transition metals such as iron. In an embodiment, an oxygen concentration (and/or concentration of other impurities) of polycrystalline source 130 is less than approximately 400 ppm by weight, and may even be less than approximately 100 ppm. Polycrystalline source 130 includes or consists essentially of AlN (or doped AlN) that is approximately stoichiometric, i.e., AlN that contains less than approximately 1% excess Al. Polycrystalline source 130 that is doped may include up

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to approximately 12% (by weight) of a dopant species such as a group IV element (e.g., Si or C), a group II element (e.g., Be or Mg) or a group VI element (e.g., O). After formation, polycrystalline source 130 may be immediately ready for subsequent sublimation-recondensation growth of single crystal AlN, and may be stored in an inert atmosphere in preparation therefor.

Production of high-purity, high-density AlN polycrystalline material

[0040] Referring to Figs. 3A-3E, a reactor 300 is utilized in the formation of polycrystalline source 130 consisting essentially of high purity, undoped AlN. Reactor 300 includes a reaction vessel 310, which is preferably fabricated of double-walled stainless steel and is water cooled. Reaction vessel 310 should be capable of a maximum internal gas pressure of approximately 45 pounds per square inch (psi), and may be evacuated, e.g., by a turbo pump 311 (backed by a mechanical pump 312) to approximately 10^{-7} Torr. A feeder mechanism 320 is connected to the top of reaction vessel 310, and may be evacuated and pressurized with the same gases and pressures as reaction vessel 310. Feeder mechanism 320 may be isolated from reaction vessel 310 by an isolation valve 322. Pellets (which may consist essentially of high (e.g., five nines) purity undoped Al and may be shaped approximately cylindrically) released from feeder mechanism 320 are directed to a crucible 330 by an upper funnel 332 and a lower funnel 334.

[0041] Crucible 330 includes a bottom plug 336 and a foil wrap 337. Bottom plug 336 may be approximately cylindrical with, e.g., a diameter of approximately 2 inches and a height of approximately 0.5 inches. Bottom plug 336 may comprise or consist essentially of W, or another high-melting-point material inert to AlN. Foil wrap 337 wraps around bottom plug 336, forming a cylinder open at the top and sealed at the bottom by bottom plug 336. Foil wrap 337 may comprise or consist essentially of W, or another high melting point material inert to AlN, and may have a thickness of approximately 0.001 inch. In an embodiment, foil wrap 337 may be wrapped around bottom plug 336 multiple times, e.g., a three-ply foil wrap 337 is formed by wrapping W foil around bottom plug 337 three times. Foil wrap 337 is held in place by wire 338. Wire 338 may comprise or consist essentially of a tungsten-rhenium alloy (e.g., 25% rhenium) and have a thickness of approximately 0.01 inch.

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[0042] Crucible 330 is disposed within a reaction zone 340 and on top of a crucible stand 342. Both reaction zone 340 and crucible stand 342 may include or consist essentially of W. Lower funnel 334 is disposed above the top opening of crucible 330, and may comprise or consist essentially of W. Lower funnel 334 is shaped to direct pellets from feeder mechanism 5 320 and upper funnel 332 into crucible 330.

[0043] Reactor 300 includes an inductive heating coil 350, which wraps around insulation 360. Insulation 360 may include or consist essentially of bubble alumina available from Zircar Ceramics, Inc. of Florida, New York held within a quartz holder. Inductive heating coil 350 may be a 10 kHz, 20 kilowatt inductive heating system available from Mesta 10 Electronics, Inc. of N. Huntingdon, Pennsylvania, and may heat to temperatures up to approximately 2300 °C. An optical pyrometer port 362 enables the measurement of temperature inside the reaction zone defined by inductive heating coil 350 by pyrometry. Gas from a series of gas tanks representatively indicated at 368 flows into reactor 300 from a bottom inlet 370 and/or a top inlet 372. The gas may comprise or consist essentially of nitrogen 15 or forming gas, and is filtered by a gas filter 374 that reduces levels of contaminants such as oxygen, water vapor, and hydrocarbons to less than 10 ppb. A vertical drive 380 is used to move crucible 330 in and out of the hot zone created by inductive heating coil 350. A conventional control station 390 includes electronic controls and power supplies for all of the components associated with reactor 300.

[0044] In order to form undoped polycrystalline source 130, pellets are cleaned in preparation for loading into feeder mechanism 320. First, the pellets are sifted (with or without water) in order to remove oddly shaped pellets or small shavings. The pellets are then ultrasonically cleaned in methanol for approximately 20 minutes, etched for approximately 7 minutes in hydrochloric acid (HCl), and rinsed several times (e.g. three times) in distilled water. 25 After another ultrasonic clean in methanol for approximately 20 minutes, the pellets are immersed in a mixture of HF and HNO₃ for approximately 2 minutes at room temperature. Finally, the pellets are rinsed in distilled water and multiple times in methanol, whereupon they may be stored in an inert or nitrogen atmosphere prior to loading in feeder mechanism 320.

[0045] Crucible 330 is loaded into reactor 300, and pellets are loaded into feeder 30 mechanism 320. Reaction chamber 310 and feeder mechanism 320 are evacuated, e.g., to a pressure less than approximately 5×10^{-5} Torr, and refilled with forming gas to a pressure of approximately 6 psi. Either nitrogen (N₂) gas or forming gas flows into reaction chamber 310

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from bottom inlet 370 and top inlet 372 at a rate of approximately 0.25 lpm. The flow of gas provides a sufficient amount of nitrogen in reaction chamber 310 to convert the pellet(s) to AlN (as described below). Inductive heating coil 350 heats crucible 330 to approximately 1900 – 2200 °C, but even higher temperatures may be utilized. In a preferred embodiment, inductive heating coil 350 heats crucible 330 to approximately 2000 – 2050 °C. Temperatures in this range have been found to be sufficient to totally react the pellets into stoichiometric AlN (which includes less than approximately 1% unreacted Al) and to drive off higher vapor pressure impurities that may be trapped within polycrystalline source 130 and create optical absorptions. The temperature at crucible 330 may be measured by pyrometry through optical pyrometer port 362. Once crucible 330 reaches the desired temperature, the temperature and gas flow conditions within reactor 300 are held constant for an approximately 3 hour pre-soak cycle. The pre-soak cleans crucible 330 and other parts of reactor 300 of contaminants, e.g., oxides, before the introduction of the Al pellets.

[0046] A reaction cycle is then performed to form undoped polycrystalline source 130. Pellets are dropped from feeder mechanism 320, through upper funnel 332 and lower funnel 334, into crucible 330. The pellets may each weigh approximately 0.23 gram, and may be dropped at a rate of approximately 1 every 90 seconds. Feeder mechanism 320 may incorporate an optical counter that counts actual pellet drops and may cycle feeder mechanism 320 to drop an additional pellet in case of a loading error. The pellets land on bottom plug 336 (or the portion of polycrystalline source 130 already produced thereon), melt, and react with the nitrogen gas to form undoped polycrystalline source 130. Each subsequent pellet dropped from feeder mechanism 320 reacts and increases the size and volume of polycrystalline source 130. In an embodiment, substantially all of each pellet reacts to form polycrystalline source 130. After a desired number of pellets are reacted to form polycrystalline source 130, the reaction gas flow rate and temperature are maintained for approximately 1 hour to ensure that the reaction is complete.

[0047] After the reaction cycle, crucible 330 (and polycrystalline source 130) is cooled down to approximately room temperature over approximately 1 hour at a positive nitrogen pressure. Thus formed, polycrystalline source 130 may weigh up to approximately 155 grams, and consists essentially of high-purity, undoped AlN. In an embodiment, an oxygen concentration (and/or concentration of other impurities such as boron or transition metals) of polycrystalline source 130 is less than approximately 400 ppm by weight, and may even be less

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than approximately 100 ppm. Polycrystalline source 130 includes or consists essentially of AlN that is approximately stoichiometric, i.e., AlN that contains less than approximately 1% excess Al. After formation, polycrystalline source 130 may be immediately ready for subsequent sublimation-recondensation growth of single crystal AlN, and may be stored in an inert atmosphere in preparation therefor.

Formation of Single-Crystal AlN

[0048] Once doped or undoped polycrystalline source 130 has been fabricated by one of the techniques described above with reference to Figs. 2A and 2B and 3A-3E, it can be utilized in the sublimation-recondensation growth of single-crystal AlN as described above with reference to Fig. 1. Because polycrystalline source 130 is approximately stoichiometric AlN with low concentrations of impurities, it may be used to form AlN crystal 120 without further preparation. Polycrystalline source 130 is separated from bottom plug 230 (or bottom plug 336), but foil wrap 240 (or foil wrap 337) remains proximate and in contact with polycrystalline source 130. Foil wrap 240 (or foil wrap 337) may remain in contact with polycrystalline source 130 and placed in crystal growth enclosure 100. Since foil wrap 240 (or foil wrap 337) is formed of W or other material inert to AlN, it does not react with or contaminate AlN crystal 120 during its formation. In an embodiment, polycrystalline source 130, surrounded by foil wrap 240 (or foil wrap 337) may be broken into smaller pieces, and one or more of them may be utilized separately to form AlN crystal 120. In this embodiment, pieces of foil wrap 240 (or foil wrap 337) may remain in contact with the pieces of polycrystalline source 130. In another embodiment, foil wrap 240 (or foil wrap 337) may be formed of the same material as crystal growth enclosure 100, e.g., W.

[0049] Referring to Fig. 4, after formation of AlN crystal 120, wafer 400 may be separated from AlN crystal 120 by the use of, e.g., a diamond annular saw or a wire saw. In an embodiment, a crystalline orientation of wafer 400 may be within approximately 2° of the (0001) face (i.e., the c-face). Such c-face wafers may have an Al-polarity surface or an N-polarity surface, and may subsequently be prepared as described in U.S. Patent No. 7,037,838 or U.S. Patent Application Serial No. 11/448,595, the entire disclosures of which are hereby incorporated by reference. In other embodiments, wafer 400 may be oriented within approximately 2° of an m-face or a-face orientation (thus having a non-polar orientation) or may have a semi-polar orientation if AlN crystal 120 is cut along a different direction. The

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surfaces of these wafers may also be prepared as described in U.S. Patent No. 7,037,838.

Wafer 400 may have a roughly circular cross-sectional area with a diameter of greater than approximately 2 cm. In an alternate embodiment, a surface area of wafer 400 may be greater than approximately 1 cm², or even greater than approximately 3 cm², and may be shaped like a quadrilateral or other polygon. A thickness of wafer 400 may be greater than approximately 100 μm, greater than approximately 200 μm, or even greater than approximately 2 mm. Wafer 400 preferably has the properties of AlN crystal 120, as described herein.

[0050] When a doped polycrystalline source 130 including a dopant species is used to form AlN crystal 120, AlN crystal 120 and wafer 400 may both incorporate the dopant species at a concentration greater than approximately 10¹⁶ /cm³. Depending on the particular dopant species, AlN crystal 120 and/or wafer 400 may exhibit n-type or p-type conductivity. In an embodiment, an oxygen concentration (and/or concentration of other impurities such as boron or transition metals such as iron) of AlN crystal 120 and/or wafer 400 is less than approximately 400 parts per million by weight (ppm), and may even be less than approximately 100 ppm. The oxygen concentration may also be less than approximately 4.5 × 10¹⁹ /cm³, or even less than 1 × 10¹⁹ /cm³, as measured by dynamic SIMS. A conductivity of AlN crystal 120 and/or wafer 400 at room temperature may be greater than approximately 10⁻⁴ Ω⁻¹cm⁻¹, or even greater than approximately 10⁻² Ω⁻¹cm⁻¹. A thermal conductivity of AlN crystal 120 and/or wafer 400 may be greater than approximately 250 Watts per meter-Kelvin (W/m·K), a value preferably measured by the American Society for Testing and Materials (ASTM) Standard E1461-01 (Current Industry Standard Test Method for Thermal Diffusivity of Solids by the Laser Flash Method), and provided by a commercial vendor such as NETZSCH Inc. of Exton, Pennsylvania. Finally, low impurity concentrations and control of the Al and N vacancy concentrations may result in an optical absorption coefficient of AlN crystal 120 and/or wafer 400 less than 100 /cm at a wavelength range of approximately 210 nanometers (nm) to approximately 480 nm. In particular, the low oxygen content of AlN crystal 120 and wafer 400 may enable an optical absorption coefficient of less than 100 /cm at a wavelength of 280 nm, as absorption at this wavelength has been ascribed to oxygen contamination (see, for example, G.A. Slack, L.J. Schowalter, D. Morelli, J.A. Freitas Jr., J. Crystal Growth **246**, 287 (2002), the entire disclosure of which is hereby incorporated by reference).

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Vapor Pressures of AlN and Si₃N₄

[0051] The relative Si, Al, and N₂ vapor pressures as a function of temperature strongly affect growth of Si-doped AlN crystals. These vapor pressures can be calculated from the JANAF tables (M.W. Chase, Jr., *Journal of Physical and Chemical Reference Data*,
 5 Monograph No. 9, NIST-JANAF Thermochemical Tables, Fourth edition (1998)), the entire disclosure of which is hereby incorporated by reference. The AlN evaporates congruently as Al atoms and N₂ molecules with very small traces of Al₂ and AlN vapor molecules. If there is any Si₃N₄ in the source, then, at a temperature of 2300°C that is typically used for growing AlN, the nitrogen pressure over Si₃N₄ solid is 53 bars. Accordingly, the decomposition pressure of solid
 10 Si₃N₄ is substantially higher than that of solid AlN. When a small amount of either Si or Si₃N₄ is dissolved in AlN, however, the Si vapor pressure is much reduced. If the crystal composition is AlN_{1-x}Si_x, then the total pressure of Si in the gas phase is roughly $P(\text{Si}) = x \times P(\text{Al})$. This is due to the fact that the Si to Al ratio in the equilibrium gas phase is the same as in the solid.

[0052] The partial pressure of Al vapor over AlN in 1 bar of N₂ at 2300°C is 0.09 bars.
 15 If x is 0.10, then $P(\text{Si}) = 0.009$ bar. This is about the same as the Si partial pressure over Si₃N₄ at this temperature, which is 0.008 bar. During crystal growth, the N₂ pressure over the AlN is typically kept between 0.5 and 10 bar, with 1.2 bar being preferred. This nitrogen pressure is much less than the N₂ pressure of 53 bars needed to form solid Si₃N₄. Thus, no Si₃N₄ is formed under these conditions. The Si atoms are transported to the growing Al crystal as mostly Si₁
 20 atoms (over 80%) although some transport may be expected as SiN, Si₂N, Si₂ and Si₃ gas-phase molecules. Undoped AlN will grow very close to stoichiometric. The nitrogen vacancy (V_N) concentration depends on the growth temperature and the nitrogen pressure; for growth at 2300°C, the aluminum nitride grows as Al₁N_{1-y}(V_N)_y, where y may be $\sim 10^{-4}$ at 1 bar N₂.

Silicon-Doped AlN Crystals

25 [0053] After making silicon-doped AlN ceramic by reacting Al-Si alloys with nitrogen, this material may be used to grow crystals by the evaporation-recondensation or solid-gas-solid technique. Tungsten crucibles are typically employed for growing AlN; as explained herein, the same crucibles may be used for growing Si-doped AlN crystals if the nitrogen pressure is between 0.5 to 10 bar and the temperature is 2000°C to 2300°C. The Si-W system possesses
 30 two intermediate compounds: WSi₂ (melting point (m.p.) 2160°C) and W₅Si₃ (m.p. 2320°C). The partial pressure of Si in the gas phase is preferably maintained low enough to prevent the

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formulation of these phases at the growth temperature. For Si/Al ratios of up to 0.1 (10%), substantially no reaction of Si with the tungsten should occur although there may be some absorption of Si by a tungsten crucible.

[0054] Thus, to achieve higher doping levels and/or to increase the fraction of Si that is

5 captured in the growing crystal from a Si-doped AlN ceramic, it may be desirable to use a crucible constructed of an alternative material. See, e.g., G.A. Slack, J. Whitlock, K. Morgan, and L.J. Schowalter, *Mat. Res. Soc. Proc.* **798**, Y10.74.1 (2004), the entire disclosure of which is hereby incorporated by reference. In an embodiment a TaC crucible (prepared as described in U.S. Patent Application Serial No. 10/822,336, the entire disclosure of which is hereby
10 incorporated by reference) is used, as it may not react with either the AlN or Si₃N₄, nor with the Al and Si vapors, in the temperature range of approximately 1800 °C to approximately 2300 °C and nitrogen pressures from approximately 1 bar to 60 bars.

Treated and Untreated Crystals

[0055] In analogy with the AlN-Al₂O₃ system where Al₂O₃ plus an Al vacancy enters
15 the AlN lattice as Al₂V_{Al}O₃, at high concentrations of Si, one expects to obtain a mixed crystal of AlN-Si₃V_{Al}N₄, with each Si₃N₄ molecule introducing one Al atom vacancy. Unfortunately, the introduction of Al vacancies will introduce acceptor levels which will compensate the Si donor levels. Thus, it is desirable to suppress the formation of Si₃V_{Al}N₄ in the AlN crystal.

[0056] In thin epitaxial layers of AlN grown on diamond substrates with Si doping in
20 this range by R. Zeisel, et al., *Phys. Rev.* **B61**, R16283 (2000), the entire disclosure of which is hereby incorporated by reference, the apparent activation energy for conduction was shown to vary from about 100 to 600 meV with the material becoming less conducting as the Si concentration increases. Zeisel et al. suggested that Si impurities in AlN to form a DX-center that has a high activation energy. However, C.G. Vande Walle, *Phys. Rev.* **B57** R2033 (1998)
25 and C.G. Vande Walle, et al. *MRS Internet J. Nitride Semicond. Res.* **4S1**, G10.4 (1999), the entire disclosures of which are hereby incorporated by reference, have shown that Si in AlN does not form such centers and typically stays centered on an Al lattice site. The decrease observed in the electrical activity of the Si by Zeisel et al. may be caused by an increasing concentration of Al vacancies as the Si content increases. This agrees with the simple idea that
30 Si atoms enter the AlN lattice as Si₃V_{Al}N₄ in order to maintain charge neutrality. Here V_{Al} designates an aluminum atom vacancy. In accordance with this latter model, then one may

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activate the Si by generating nitrogen vacancies in the AlN lattice. The nitrogen vacancies will tend to convert the Si_3N_4 to SiN by combining with aluminum vacancies to form voids. When the conversion is complete, nearly all of the Si atoms should be electrically active.

[0057] Ideally, the doped AlN crystal is grown under conditions which generate nitrogen vacancies as described above. However, it is also possible to anneal AlN crystal 120 after growth by reducing the nitrogen partial pressure in vapor mixture 110 above the crystal while keeping crystal growth enclosure 100 in nearly an isothermal environment at a temperature above 1800 °C. Crystal growth enclosure 100 may be made from W, but alternative crucible materials, such as TaC, may be preferred to reduce the loss of dopant (e.g., Si) through its walls.

[0058] If AlN crystals with Si concentrations greater than $1.3 \times 10^{21} \text{ cm}^{-3}$ are grown, then, according to Hermann et al., *Appl. Phys. Letters* 86 192108 (2005), the entire disclosure of which is hereby incorporated by reference, the crystals will be electrically degenerate and the resistivity can be as low as 2 to 3 $\Omega\text{-cm}$ at room temperature. Even lower resistivities are possible if the formation of V_{Al} can be suppressed as described herein.

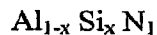
Annealing Treatments

[0059] Annealing treatments may be employed as a means of controlling the nitrogen vacancy content, aluminum vacancy content, and/or dopant electrical activation in wafer 400 cut from AlN crystal 120. Exemplary AlN crystal 120 doped with Si is grown at nitrogen pressures between 0.5 and 10 bars; lower N_2 pressures may significantly slow the growth rate or suppress it entirely. Once grown, however, some of the nitrogen may be extracted from AlN crystal 120 or wafer 400, i.e., nitrogen vacancies may be injected into the material. Wafer 400 may be annealed at a temperature greater than approximately 1900°C in order to electrically activate a dopant species therein. The annealing may also decrease a concentration of Al vacancies and/or increase a concentration of N vacancies in wafer 400.

[0060] As the N_2 pressure is reduced around the crystal at approximately 1900 °C or above, the nitrogen diffuses out. In an embodiment, a suitable N_2 pressure at temperature T for creating the maximum number of N vacancies is greater than the pressure required to form AlN from Al at the same temperature T. For example, for an annealing temperature of 2000 °C, a suitable N_2 pressure used during annealing may be selected from the range of approximately 2 millibar (mbar) to approximately 0.5 bar. The N_2 pressure may be less than approximately

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twice a N_2 pressure required to form AlN from Al at temperature T. In an embodiment, the N_2 pressure used during annealing is selected from the range of approximately 0.1 mbar and approximately 5 bars. Higher pressures may generally be preferred at higher temperatures. In another embodiment, an inert gas such as argon (Ar) is introduced during the annealing to suppress Al evaporation as discussed below. The reduction of " Si_3N_4 " in solution in the AlN crystal to form SiN happens before the decomposition of Al_1N_1 to $Al_1N_{1-\epsilon}$, where ϵ is the nitrogen loss expected in undoped AlN. The Al vacancies and nitrogen vacancies can combine and be replaced by lattice voids or surface pits and the chemical composition becomes:



Essentially the Si is now present as SiN and is thus electrically active as a donor. When it was present as Si_3N_4 , it was electrically inactive. After annealing, substantially all of a dopant species (such as Si) present in wafer 400 may be electrically activated. A conductivity of annealed wafer 400 may be greater than approximately $10^{-4} \Omega^{-1}cm^{-1}$, or even greater than approximately $10^{-2} \Omega^{-1}cm^{-1}$, at room temperature.

Making N-Type AlN Using Only Nitrogen Vacancies

[0061] Annealing may generate enough nitrogen vacancies in undoped AlN so that the electron donors are the excess Al atoms. In this case, one may anneal undoped wafer 400 in a low N_2 gas pressure at temperatures between 1700°C and 2200°C. During the anneal, some of the nitrogen in the AlN will diffuse out to the surface and escape, leaving the Al behind. This is preferably done in a flowing argon-nitrogen atmosphere at a total pressure within the range of approximately 2 bars to approximately 30 bars. The argon prevents the Al from evaporating. The nitrogen pressure is just enough to keep the AlN from converting back to metallic aluminum. That is, the pressure of N_2 is greater than the N_2 pressure required to form AlN from Al at the anneal temperature. Annealed undoped wafer 400 (consisting essentially of AlN with no extrinsic electron-donating dopants) may have a conductivity greater than approximately $10^{-2} \Omega^{-1}cm^{-1}$ at room temperature. Such conductivity may be supplied by excess Al atoms (equivalently, by nitrogen vacancies) in the AlN lattice.

[0062] It will be seen that the techniques described herein provide a basis for production of undoped and doped crystals including AlN and AlGaN. The terms and expressions employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the

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features shown and described or portions thereof. Instead, it is recognized that various modifications are possible within the scope of the invention claimed.

[0063] What is claimed is:

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- 1 1. A method of forming polycrystalline AlN, the method comprising the steps of:
2 providing within a crucible a pellet comprising Al; and
3 reacting the pellet at a reaction temperature and a reaction pressure with nitrogen gas to
4 form a polycrystalline AlN ceramic,
5 wherein the polycrystalline AlN ceramic is approximately stoichiometric.
- 1 2. The method of claim 1, wherein the pellet consists essentially of Al.
- 1 3. The method of claim 2, wherein the reaction temperature is within the range of
2 approximately 1900 °C to approximately 2200 °C.
- 1 4. The method of claim 1, wherein the pellet comprises a first concentration of a dopant
2 species.
- 1 5. The method of claim 4, wherein the dopant species comprises Si.
- 1 6. The method of claim 4, wherein the first concentration is less than approximately 12%
2 by weight.
- 1 7. The method of claim 4, wherein the polycrystalline AlN ceramic comprises a second
2 concentration of the dopant species.
- 1 8. The method of claim 7, wherein the second concentration is less than approximately
2 12% by weight.
- 1 9. The method of claim 4, wherein the reaction temperature is within the range of
2 approximately 1600 °C to approximately 2200 °C, and the reaction pressure is within the range
3 of approximately 1 bar to approximately 60 bars.
- 1 10. The method of claim 1, wherein an oxygen concentration of the polycrystalline AlN
2 ceramic is less than approximately 400 ppm.
- 1 11. The method of claim 10, wherein the oxygen concentration of the polycrystalline AlN
2 ceramic is less than approximately 100 ppm.
- 1 12. The method of claim 1, wherein substantially all of the pellet is reacted.

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- 1 13. The method of claim 1, further comprising:
2 providing within the crucible at least one additional pellet comprising Al; and
3 reacting the at least one additional pellet at the reaction temperature and the reaction
4 pressure with nitrogen gas, thereby increasing a volume of the polycrystalline AlN ceramic.
- 1 14. The method of claim 1, further comprising:
2 providing the polycrystalline AlN ceramic at a first end of and within a crystal growth
3 enclosure;
4 subliming the polycrystalline AlN ceramic at a formation temperature; and
5 forming an AlN single crystal at a second end of the crystal growth enclosure.
- 1 15. The method of claim 14, wherein the formation temperature is within the range of
2 approximately 2000°C to approximately 2750 °C.
- 1 16. The method of claim 14, wherein an oxygen concentration of the AlN single crystal is
2 less than approximately 400 ppm.
- 1 17. The method of claim 16, wherein the oxygen concentration of the AlN single crystal is
2 less than approximately 100 ppm.
- 1 18. The method of claim 14, wherein an oxygen concentration of the AlN single crystal is
2 less than approximately $4.5 \times 10^{19} / \text{cm}^3$.
- 1 19. The method of claim 14, wherein a thermal conductivity of the AlN single crystal is
2 greater than approximately 250 W/m·K.
- 1 20. The method of claim 14, wherein the polycrystalline AlN ceramic comprises a dopant
2 species, and the AlN single crystal comprises the dopant species at a first concentration.
- 1 21. The method of claim 20, wherein the dopant species comprises Si.
- 1 22. The method of claim 20, wherein the first concentration is greater than approximately
2 $10^{16} / \text{cm}^3$.
- 1 23. The method of claim 14, wherein the AlN single crystal has a conductivity greater than
2 approximately $10^{-4} \Omega^{-1} \text{cm}^{-1}$ at room temperature.

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1 24. The method of claim 14, wherein at least a portion of the crucible is disposed proximate
2 and in contact with the polycrystalline AlN ceramic.

1 25. A method of forming a doped AlN wafer, the method comprising the steps of:
2 providing a single-crystal wafer comprising AlN and a dopant species; and
3 annealing the single-crystal wafer to electrically activate the dopant species.

1 26. The method of claim 25, wherein the dopant species comprises Si.

1 27. The method of claim 25, wherein the step of annealing decreases a concentration of
2 aluminum vacancies in the single crystal wafer.

1 28. The method of claim 25, wherein the step of annealing increases a concentration of
2 nitrogen vacancies in the single-crystal wafer.

1 29. The method of claim 25, wherein the step of annealing is performed at an annealing
2 temperature and an annealing nitrogen pressure, and the annealing nitrogen pressure is greater
3 than approximately a nitrogen pressure required to form AlN from Al at the first temperature.

1 30. The method of claim 29, wherein the annealing nitrogen pressure is less than
2 approximately twice the nitrogen pressure required to form AlN from Al at the first
3 temperature.

1 31. The method of claim 30, wherein the annealing nitrogen pressure is within the range of
2 approximately 0.1 mbar to approximately 5 bars.

1 32. The method of claim 29, wherein the annealing temperature is greater than
2 approximately 1900 °C.

1 33. The method of claim 25, wherein after annealing the single-crystal wafer has a
2 conductivity greater than approximately $10^{-4} \Omega^{-1}\text{cm}^{-1}$ at room temperature.

1 34. The method of claim 33, wherein after annealing the single-crystal wafer has a
2 conductivity greater than approximately $10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature.

1 35. A method of forming an AlN wafer, the method comprising the steps of:

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2 providing a single-crystal wafer comprising undoped AlN and having a first
3 conductivity; and

4 annealing the single-crystal wafer in an ambient at an annealing temperature and an
5 annealing pressure,

6 wherein after annealing the single-crystal wafer has a second conductivity greater than
7 the first conductivity.

1 36. The method of claim 35, wherein the annealing temperature is within the range of
2 approximately 1700 °C to approximately 2200 °C.

1 37. The method of claim 35, wherein the annealing pressure is within the range of
2 approximately 2 bars to approximately 30 bars.

1 38. The method of claim 35, wherein the ambient consists essentially of nitrogen and at
2 least one inert gas.

1 39. The method of claim 38, wherein the at least one inert gas comprises argon.

1 40. The method of claim 38, wherein a pressure of the nitrogen in the ambient is greater
2 than a nitrogen pressure required to form AlN from Al at the annealing temperature.

1 41. The method of claim 35, wherein the second conductivity is greater than approximately
2 $10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature.

1 42. An AlN single crystal having a thickness greater than approximately 100 μm , a cross-
2 sectional area greater than approximately 1 cm^2 , and a conductivity greater than approximately
3 $10^{-4} \Omega^{-1}\text{cm}^{-1}$ at room temperature.

1 43. The AlN single crystal of claim 42, further comprising a substitutional dopant species
2 and exhibiting n-type conductivity.

1 44. The AlN single crystal of claim 43, wherein the substitutional dopant species comprises
2 a group IV element.

1 45. The AlN single crystal of claim 44, wherein the substitutional dopant species comprises
2 Si.

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1 46. The AlN single crystal of claim 42 consisting essentially of AlN and nitrogen vacancies.

1 47. The AlN single crystal of claim 42, wherein the thickness is greater than approximately
2 200 μm .

1 48. The AlN single crystal of claim 47, wherein the thickness is greater than approximately
2 2 mm.

1 49. The AlN single crystal of claim 42, wherein the conductivity is greater than
2 approximately $10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature.

1 50. The AlN single crystal of claim 42, wherein a thermal conductivity thereof is greater
2 than approximately 250 W/m·K.

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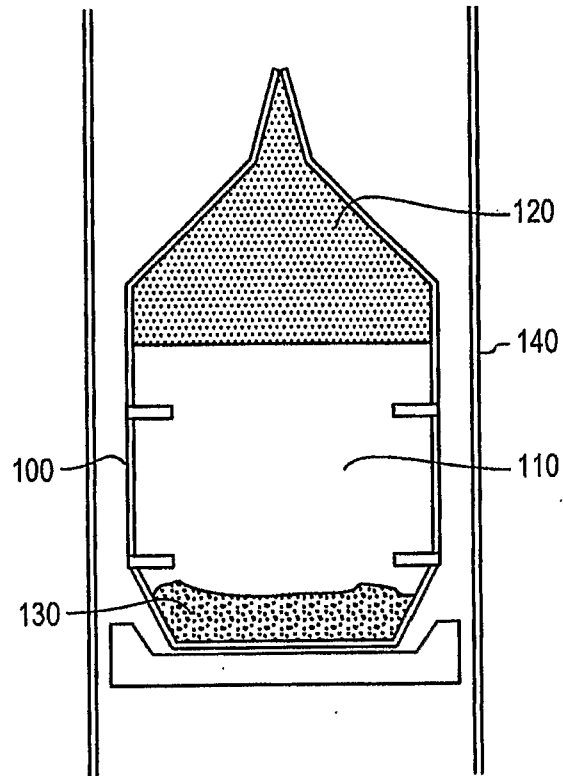


FIG. 1

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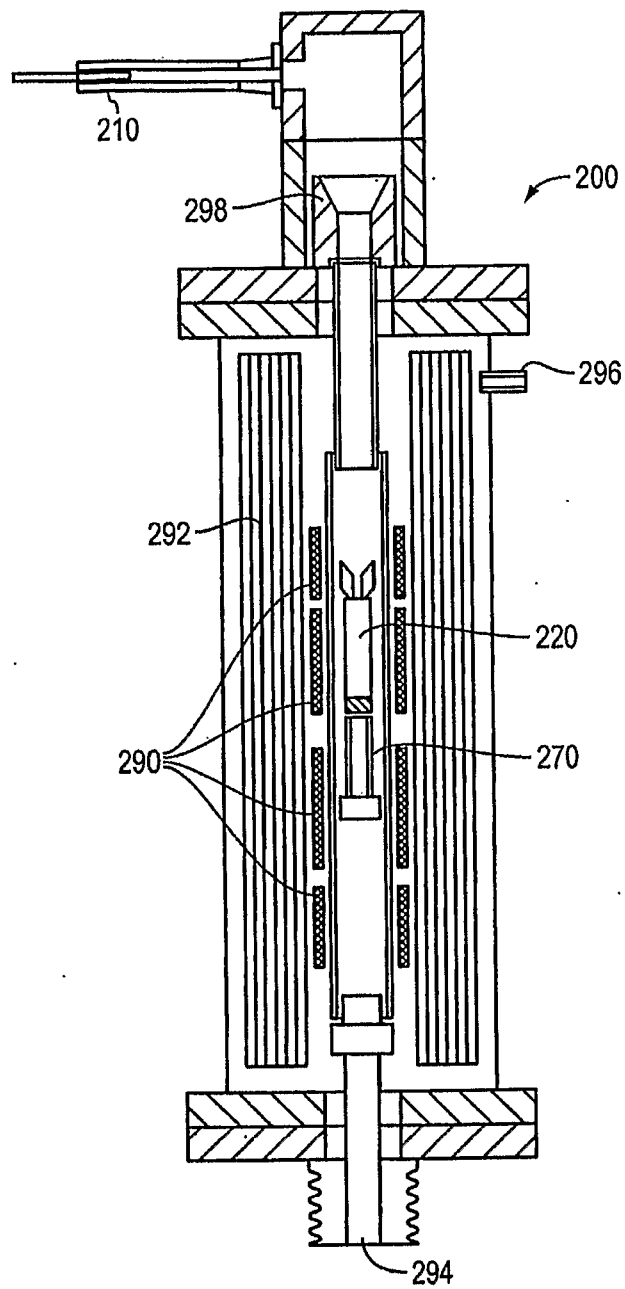


FIG. 2A

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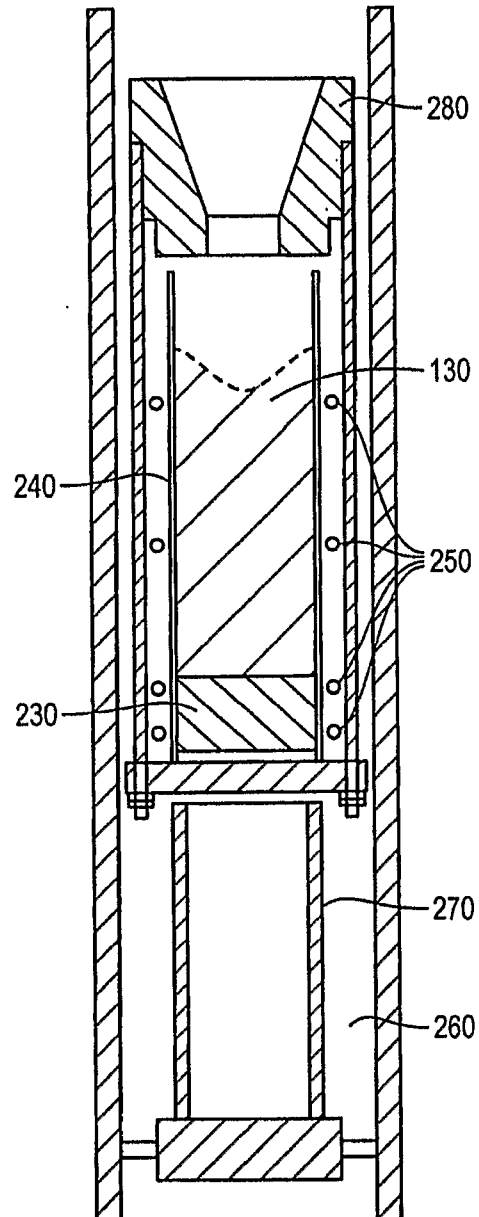


FIG. 2B

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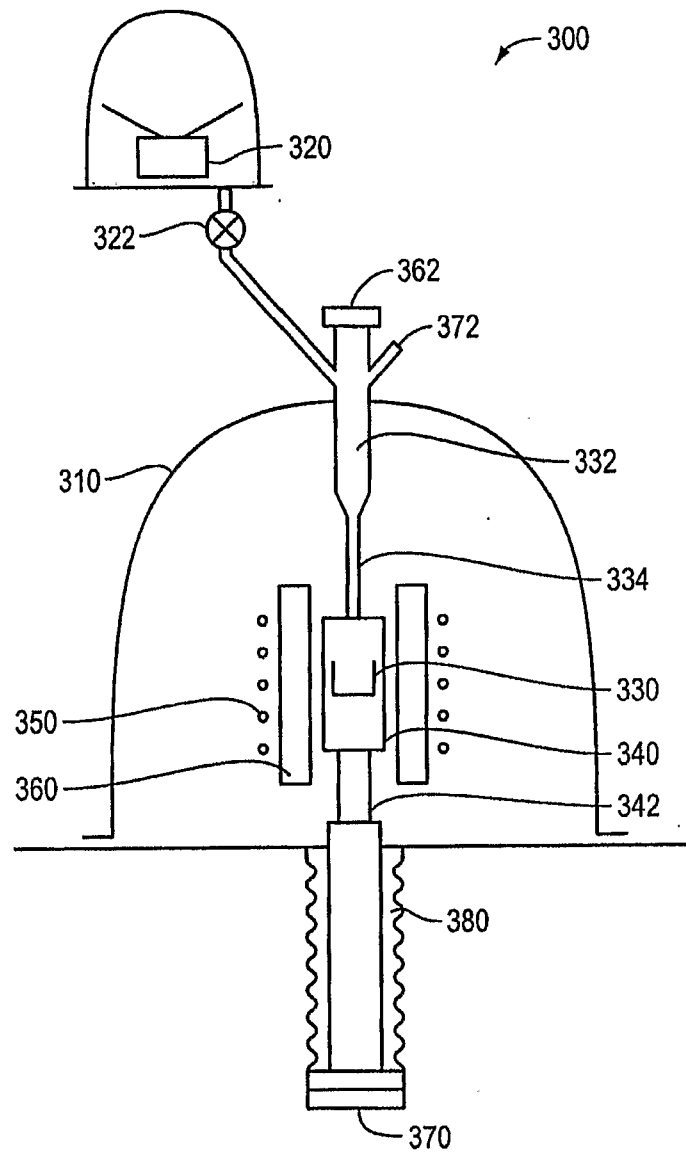


FIG. 3A

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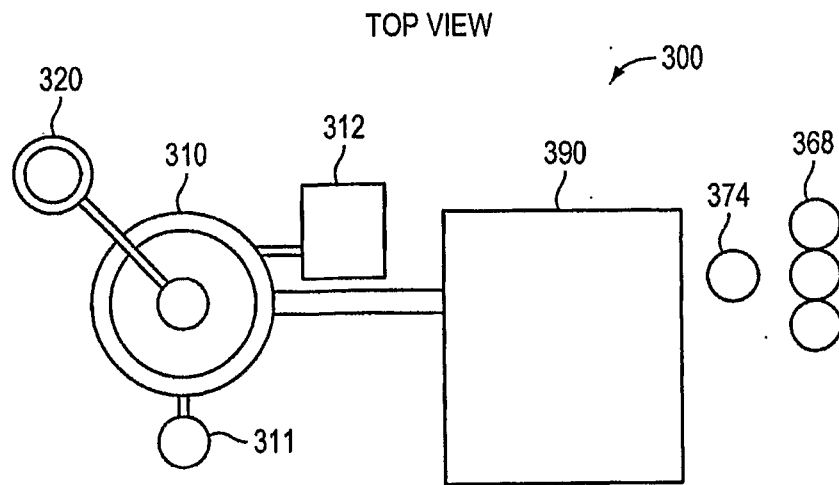


FIG. 3B

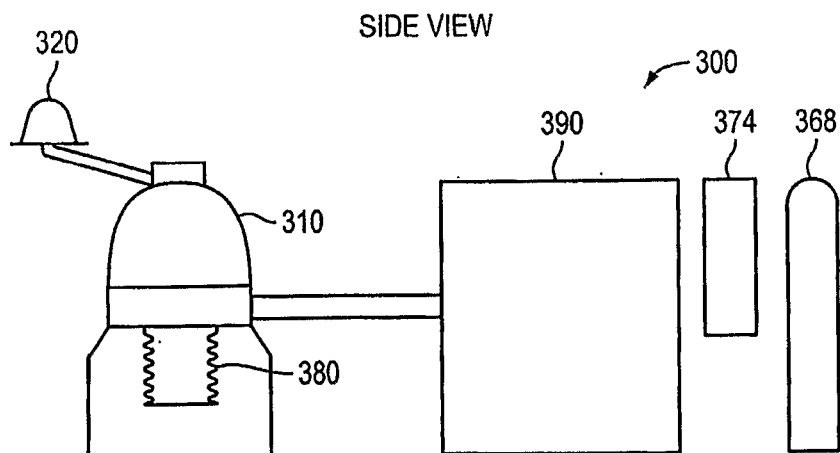


FIG. 3C

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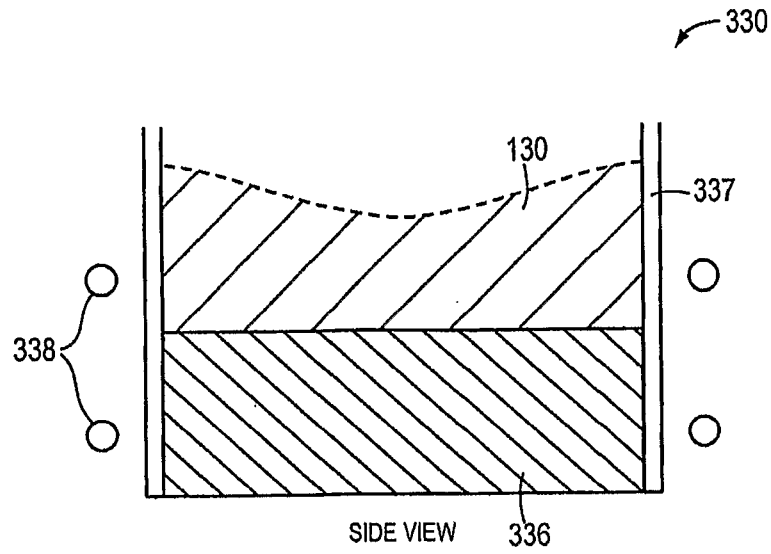
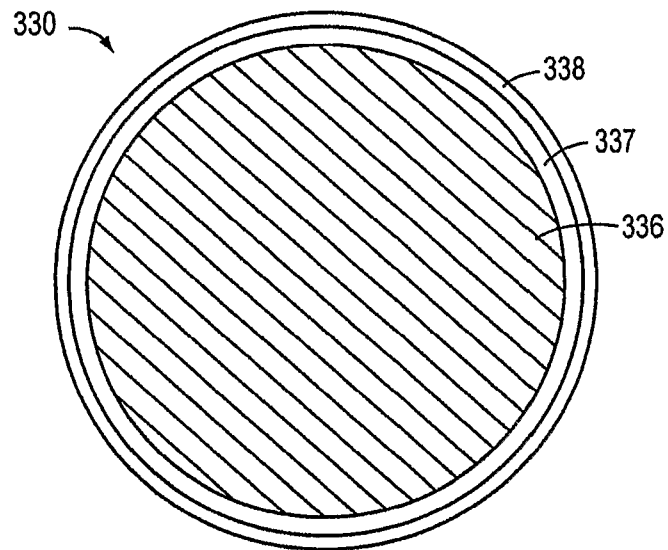


FIG. 3D



TOP VIEW

FIG. 3E

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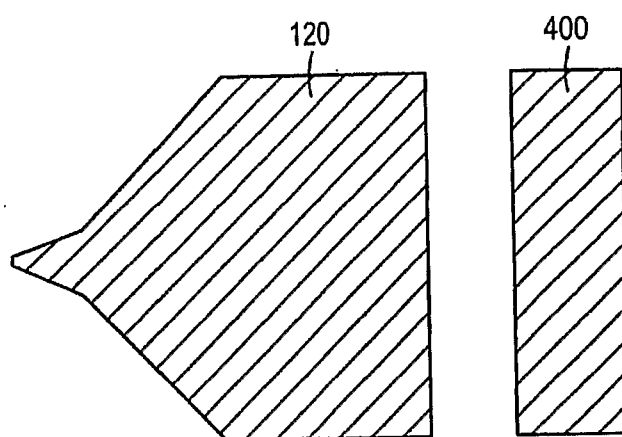


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/007980

A. CLASSIFICATION OF SUBJECT MATTER
INV. C30B29/40 C30B23/00 C30B33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C30B C04B

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, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SLACK ET AL: "AIN single crystals" JOURNAL OF CRYSTAL GROWTH, ELSEVIER, AMSTERDAM, NL, no. 42, December 1977 (1977-12), pages 560-563, XP002077480 ISSN: 0022-0248	1-3, 10, 12-16, 42
Y	page 560, column 1, paragraph 2 page 561, paragraph 2 - page 562, paragraph 1; figures 1,3 ----- -/--	4-8

☒ 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.

Z document member of the same patent family

Date of the actual completion of the international search

4 October 2007

Date of mailing of the international search report

12/10/2007

Name and mailing address of the ISA/

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Ruiz Martinez, Maria

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/007980

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SLACK G A ET AL: "Growth of high purity AIN crystals" JOURNAL OF CRYSTAL GROWTH, ELSEVIER, AMSTERDAM, NL, vol. 34, 1976, pages 263-279, XP002971531 ISSN: 0022-0248 abstract page 268, column 2, line 13 - line 19 page 270, column 1, paragraph 2 page 275, column 2, line 27 - line 32 -----	4-8
A	DE 102 48 964 A1 (BICKERMANN MATTHIAS [DE]) 22 April 2004 (2004-04-22) claims 1,5 page 4, column 2, line 22 - line 37 page 5, column 1, line 22 - line 38 -----	14,15, 20,21
X	US 5 494 861 A (YAMAGA SHIGEKI [JP] ET AL) 27 February 1996 (1996-02-27) claim 1 -----	25
X	US 5 520 785 A (EVANS KEENAN L [US] ET AL) 28 May 1996 (1996-05-28) claims 1-3,7,8; figure 2 -----	35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/007980

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-24,42-50

Method of forming polycrystalline AlN starting material for
producing AlN single crystal

2. claims: 25-41

Annealing of AlN wafer

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/007980

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 10248964	A1	22-04-2004	NONE	
US 5494861	A	27-02-1996	DE 4438398 A1	04-05-1995
			JP 2875726 B2	31-03-1999
			JP 7122570 A	12-05-1995
US 5520785	A	28-05-1996	NONE	