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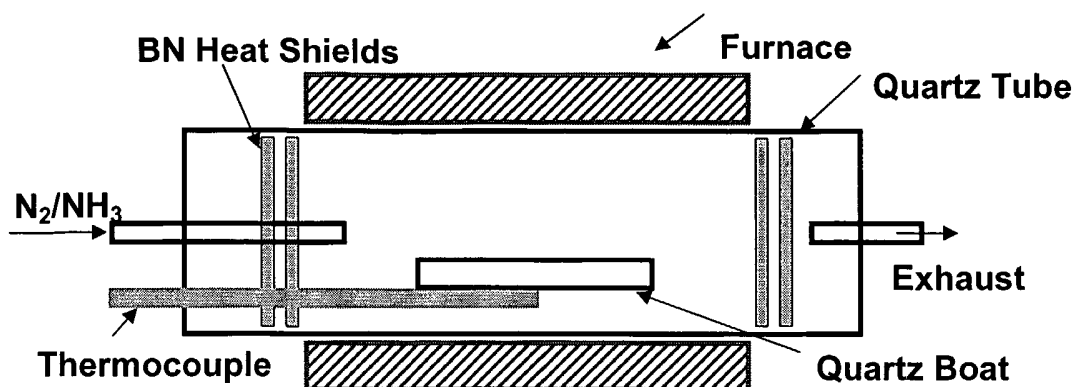
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(54) Title: METHOD OF MAKING GROUP III NITRIDES



(57) **Abstract:** The present invention provides a novel high-yielding process for preparing high purity Group III nitrides. The process involves heating a Group III metal and a catalytic amount of a metal wetting agent in the presence of a nitrogen source. Group III metals can be stoichiometrically converted into high purity Group III nitride powders in a short period of time. The process can provide multi-gram quantities of high purity Group III nitrides in relatively short reaction times. Detailed characterizations of GaN powder were performed and are reported herein, including morphology and structure by SEM and XRD, optical properties by cathodoluminescence (CL), and Raman spectra to determine the quality of the GaN particles. The purity of GaN powder was found to be greater than 99.9% pure, as analyzed by Glow Discharge Mass Spectrometry (GDMS). Green, yellow, and red light emission can be obtained from doped GaN powders.

Method of Making Group III Nitrides

Related Applications

This application is a continuation-in-part based on co-pending Provisional Application Serial No. 60/586,545 and co-pending Provisional Application Serial No. 60/632,275, the disclosures of which are incorporated by reference.

Field of the Invention

The field of the invention relates to coatings and semiconductor materials, more specifically the preparation of Group III nitride compositions.

Background of the Invention

Commercial gallium nitride (GaN) is typically synthesized through the reaction of gallium oxide (Ga_2O_3) with ammonia (NH_3), which results in GaN with a high concentration of residual oxygen. High impurity concentrations increases the density of dislocations in GaN single crystals and inhibits continuous growth. Commercial powders made from metal gallium (Ga) are extremely expensive and the quantity available is limited because the yield of current processes is low.

Gallium nitride in the wurtzite form has a large direct band gap of 3.45 eV at room temperature. GaN also forms a continuous range of solid solutions with aluminum nitride (AlN) (6.28 eV) and indium nitride (InN) (1.95 eV). Thus, Group III-nitrides, and gallium nitride in particular, are very attractive for use in opto-electronic devices because any band gap with energy in this range, from the visible to the deep UV, is theoretically achievable with these materials. Opto-electronic devices are currently fabricated by growing GaN on hetero-substrates such as sapphire, SiC, ZnO, Al_2O_3 , LiGaO_2 , and LiAlO_2 . The mismatches in lattice parameters and thermal expansion coefficients result in high dislocation densities in these films.

Group III nitrides are widely known to emit light ranging from UV to the visible spectra. Many group III nitrides therefore show potential as opto-electronic light sources (S. Nakamura, et al., *Jpn. J. Appl. Phys.* **1996**, 35, L217) and high frequency power devices (M. A. Kahn, et al. *Appl. Phys. Lett.* **1993**, 63, 1214). For example, gallium nitride powder can be used to make optical displays by utilizing the fluorescent properties of GaN crystals (see K. Hara,

U.S. Patent Application Publication No. 2003/0226497 A1). Group III nitrides can be valuable in combination with ceramics, particularly the aluminum nitrides (see “A study of the physical properties and electrochemical behavior of AlN films”, F. Vacandio, Y. Massiani, P. Gravier, *Surf. Coat. Tech.* **1997**, 92, 221).

In order to continue and speed the development of this technology, bulk substrates are greatly desired. Bulk substrates will allow the realization of high device efficiencies, lower leakage currents, and longer device lifetimes. GaN bulk single crystals and wafers are thus greatly desired for homoepitaxial film growth. Crystal growth processes for GaN bulk growth, e.g., sublimation and high-pressure methods, demand the availability of a high purity, single-phase GaN powder.

Johnson et al. first presented the synthesis of GaN powder by flowing NH_3 over molten gallium at temperatures of 900-1000 °C (W.C. Johnson, J.B. Parsons, M.C. Crew, *J. Phys. Chem.* **1932**, 36, 2651). Later, Lorenz developed a synthetic method of preparing GaN using Ga_2O_3 and NH_3 (M.R. Lorenz, B.B. Binkowski, *J. Electrochem. Soc.* **1962**, 109, 24). In 1972, Pichugin and Yas'kov (I.G. Pichugin, D.A. Yaskov, *Inorg. Mat.* **1972**, 6, 1732) showed that GaN powder could be synthesized via the reaction: $\text{Ga}(l) + \text{NH}_3(g) = \text{GaN}(s) + 3/2\text{H}_2(g)$ where $\Delta G_r = -51 \text{ kJ/mol}$ at 800 °C. Compared to the conversion from Ga_2O_3 , the key advantage of this procedure is that GaN powder of higher purity can be obtained. GaN powder has also been synthesized by injecting NH_3 into molten Ga under atmospheric pressure in the temperature range of 900-980 °C (M. Shibata, T. Furuya, H. Sakaguchi, S. Kuma, *J. Crystal Growth* **1999**, 196, 47). There is only one report of the efficient conversion of Ga to GaN with flowing NH_3 in a horizontal furnace (C.H. Balkas, R.F. Davis, *J. Am. Ceram. Soc.* **1996**, 79, 2309).

Several research groups have demonstrated the growth of GaN powders through various other synthetic methods. Ga_2O (C. M. Balkas, R.F. Davis, *J. Am. Ceramic Soc.* **1996**, 79, 2309), and GaP or GaAs (A. Addamino, *J. Electrochem. Soc.* **1961**, 108, 1072) have been used as precursors and reacted with NH_3 to make GaN powder. Other methods have also been explored recently, such as the decomposition of organometallic compounds containing Ga and N (K.H. Kim, C.H. Ho, H. Doerr, C. Deshpandey, R.F. Bunshah, *J. Mater. Sci.* **1992**, 27, 2580), plasma synthesis (K. Baba, N. Shokata, M. Yonezawa,

Appl. Phys. Lett. **1989**, *54*, 2309), and microwave-assisted combustion methods (B. Vaidhyathan, D.K. Agrawal, R. Roy, *J. Mater. Res.* **2000**, *15*, 974). Junko disclosed a method of obtaining GaN powders by dropping an ammonia solution into gallium nitric hydrate solution to form gallium hydroxide, followed by dehydration to form gallium oxide, which was then heated under an ammonia atmosphere (Junko et al., Japanese Patent Application No. 10-373540). These processes, however, do not disclose the advantages of using a wetting agent, and more efficient and suitable processes are required by industry. Additionally, most of these methods experience either very low yields or high impurity concentrations.

Cahn first introduced the idea of interfacial wetting in 1977 (J.W. Cahn, *J. Chem. Phys.* **1977**, *66*, 3677). Cahn suggested that one component in a binary liquid mixture might segregate to the liquid surface. Recently, interfacial wetting has been observed in fluid alkali metal-alkali halide and liquid gallium-based binary alloys, such as Ga-Bi (E.B. Flom, M. Li, A. Acero, N. Maskil, S.A. Rice, *Science* **1993**, *260*, 332; H. Tostmann, E. DiMasi, O.G. Shpyrko, P.S. Pershan, B.M. Ocko, M. Deutsch, *Phys. Rev. Lett.* **2000**, *84*, 4385) and Ga-Pb (D. Chatain, P. Wynblatt, *Surf. Sci.* **1996**, *345*, 85). Bismuth has been used as surfactant in growing GaN thin films by a Molecular Beam Epitaxy (MBE) technique disclosed by Kisielowski in US Patent No. 6,379,472. Nickel-mesh has been used as a catalyst to help decrease the kinetic barrier to forming GaN (K.S. Nahm, S.H. Ahn, S.H. Lee, *IPAP Conf. Series 1*, **2000**, 30). None of these studies, however, disclose the use of bismuth, germanium, tin, or lead as a wetting agent for the preparation of Group III nitrides.

Currently, there is a need for bulk supplies of Group III nitrides, particularly high purity Group III nitrides. Few companies in the US manufacture commercial gallium nitride (GaN) powder, and the commercial powders typically contain relatively high levels of impurities. Because of the lack of highly efficient methods for the synthesis of Group III nitrides, novel preparations are highly desirable.

Additionally, recent demonstrations of visible (blue, green, red) and infrared (1.54 μm) electroluminescence from rare earth (RE) doped gallium nitride produced significant interest in Group III nitrides for potential applications in optical communications and full color displays (A. J. Steckl and

J. M. Zavada, *Mater. Res. Bull.* **1999**, 24, 33; A. J. Steckl, et al. *Compound Semicond.* **2000**, 6, 48). The properties of erbium-doped GaN and other III-V semiconductors have been reviewed by Zavada and Steckl (J. M. Zavada and D. Zhang, *Solid-State Electron.* **1995**, 38, 1285; A. J. Steckl, et al. *IEEE J. Selected Topics in Quantum Electronics*, **2002**, 8, 749) The GaN-based semiconductor structures are of great interest because they appear to be optically robust, and chemically and thermally stable. Favenne et al. reported a strong dependence of the emission intensity of the Er^{3+} ions on the band gap of the host semiconductor and on the material temperature (P. N. Favenne, et al. *Electron. Lett.* **1989**, 25, 718). The wide band-gap of GaN leads to a reduced RE emission quenching effect and the observation of strong RE emission at room temperature (*ibid*). Accordingly, novel preparations of rare earth metal-doped Group III nitride compositions are needed.

Summary of the Invention

The present invention provides a novel process for preparing high purity, single phase Group III nitrides, and in particular, gallium nitride. The invention also provides novel compounds prepared by the methods described herein. The process involves heating a Group III metal and a catalytic amount of a metal wetting agent, e.g., bismuth, in the presence of a nitrogen source, e.g., ammonia. Group III metals can be stoichiometrically converted into high purity Group III nitride powders in less than 6 hours. The process can provide hundred-gram quantities of high purity Group III nitrides in relatively short reaction times. For example, 100 grams of gallium metal was converted into 120 grams of high-purity gallium nitride powder, corresponding to a greater than 99.9% yield, in five hours of reaction time.

Detailed characterizations of gallium nitride (GaN) powder prepared by these methods were performed and are reported herein. The purity of GaN powder prepared was greater than 99.9% pure, as analyzed by Glow Discharge Mass Spectrometry (GDMS). The morphology and structure of the resulting GaN powder were investigated by SEM and XRD. The optical properties of the product were characterized by cathodoluminescence (CL). Raman spectra were measured at room temperature to determine the quality of the GaN particles. The GaN produced was high purity, hexagonal polycrystalline material, composed of plate-like grains 1 to 20 μm in diameter.

Brief Description of the Drawings

FIG. 1 illustrates a schematic view of a vertical furnace used for preparing Group III nitrides.

FIG. 2 illustrates a schematic view of a horizontal furnace used for preparing Group III nitrides.

FIG. 3 illustrates yields of gallium nitride powder plotted against reaction time under ammonia gas at 1000 °C with 5 molar % bismuth as the wetting agent.

FIG. 4 illustrates Ga-Bi Alloy wetting (a) below and (b) above $T_{crit} = 262^{\circ}\text{C}$. (Courtesy of H. Tostmann). The high density phase completely wets the exposed surface by intruding between the low density phase and the gas phase.

FIG. 5 illustrates a typical X-Ray Diffraction (XRD) pattern, using $\text{Cu } K_{\alpha}$ radiation, of GaN powder produced by the disclosed procedures after removal of bismuth. A typical $\theta - 2\theta$ scan mode XRD pattern of the powder after the removal of Bi is demonstrated.

FIG. 6 (a) illustrates a scanning electron microscopy (SEM) image of synthesized GaN powder, showing a 10 μm resolution bar.

FIG. 6 (b) illustrates a SEM image of a large GaN plate, showing a 2 μm resolution bar.

FIG. 7 illustrates a typical Cathodoluminescence (CL) spectrum of synthesized GaN powder at room temperature.

FIG. 8 shows Raman spectroscopy results of (a) commercial GaN powder vs. (b) synthesized GaN powder, each at room temperature.

FIG. 9 illustrates the XRD pattern for GaN powder produced in a boron nitride crucible after removal of the bismuth wetting agent.

FIG. 10. illustrates a representative X-ray diffraction pattern of the erbium-doped GaN powder after the removal of bismuth.

FIG. 11. illustrates an SEM image of the morphology of synthesized GaN:Er powder.

FIG. 12. illustrates a PL spectra of erbium-doped GaN powder. The PL is performed at room temperature with an argon laser line at 496.5 nm.

FIG. 13. illustrates a microprobe mapping analysis of a ~20 μm diameter erbium-doped GaN particle.

FIG. 14. illustrates the CL of GaN powder doped with 1 % Eu at room temperature. Many detailed transitions can be observed in the 530-630 nm range.

Detailed Description of the Invention

The present invention provides a novel synthetic process for preparing high purity, single phase Group III nitrides, and in particular, gallium nitride. The process involves heating a Group III metal and a catalytic amount of a metal wetting agent, e.g., bismuth, in the presence of a nitrogen source, e.g., ammonia. The Group III metals are stoichiometrically converted into high purity Group III nitride powders in less than 6 hours. The process can provide one hundred-gram quantities of high purity Group III nitrides in relatively short reaction times. For example, 100 grams of gallium metal was converted into 120 grams of high-purity gallium nitride powder, corresponding to a greater than 99.9% yield in five hours of reaction time.

Detailed characterizations of gallium nitride (GaN) powder prepared by these methods were performed and are reported herein. The purity of GaN powder prepared was greater than 99.9% pure, as analyzed by Glow Discharge Mass Spectrometry (GDMS). The morphology and structure of the resulting GaN powder were investigated by SEM and XRD. The optical properties of the product were characterized by cathodoluminescence (CL). Raman spectra were measured at room temperature to determine the quality of the GaN particles. The GaN produced was high purity, hexagonal polycrystalline material, composed of plate-like grains 1 to 20 μm in diameter.

The method for making Group III nitrides includes contacting a mixture that includes a Group III element, and one or more wetting agents, with a nitrogen atom source to form a Group III nitride composition. The wetting agents are typically selected from the group of bismuth, germanium, tin, and lead, or combinations thereof. When bismuth is used as a wetting agent, the procedure does not involve molecular beam epitaxy (MBE). MBE is optionally not employed in other embodiments of the invention.

Definitions

The following definitions are used, unless otherwise described.

A stated temperature refer to degrees Celsius at one atmosphere of pressure. The temperature of a reaction can be measured in either the gas or liquid phases. Typically, the reaction temperature is measured in the gas phase above the liquid phase, by a thermocouple placed within about 2 cm of the liquid phase.

As used herein, "nitride" refers to a compound containing a nitrogen atom covalently bonded to a more electropositive element.

As used herein, "Group III element" refers to an element that contains one electron in a p-orbital, wherein the p-orbital is the element's outermost valence orbital. The Group III elements are the elements boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl). As used herein, a Group III element can also be a composition that contains a Group III element, or a metal alloy containing a Group III element. The Group III element can be a compound containing a Group III element, such as an organometallic compound, e.g. $\text{Al}(\text{CH}_3)_3$, or an inorganic compound containing a Group III element, e.g., GaCl . Suitable Group III compounds include, e.g., halides, oxides, sulfides, hydroxides, nitrates, arsenides, antimonides and phosphides. More specifically, Group III compounds can be, e.g., (BH_3) , borane complexes such as borane-methyl sulfide complex $(\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2)$, a boron atom substituted with one or more alkyl groups, BCl_3 , BBr_3 , BF_3 , BI_3 , B_2O_3 , $\text{B}(\text{OH})_3$, $\text{B}(\text{NO}_3)_3$, BP , an aluminum atom substituted with one or more alkyl groups, AlCl_3 , AlBr_3 , AlI_3 , Al_2O_3 , Al_2S_3 , $\text{Al}(\text{OH})_3$, $\text{Al}(\text{NO}_3)_3$, AlAs , AlP , a gallium atom substituted with one or more alkyl groups, GaCl , GaCl_2 , GaCl_3 , GaBr , GaBr_3 , GaF_3 , GaI , GaI_3 , Ga_2O , Ga_2O_3 , Ga_2S_3 , $\text{Ga}(\text{OH})_3$, $\text{Ga}(\text{NO}_3)_3$, GaAs , GaP , GaSb , GaS , Ga_2S , an indium atom substituted with one or more alkyl groups, InCl , InCl_2 , InCl_3 , InBr , InBr_3 , InF_3 , InI , InI_3 , In_2O , In_2O_3 , $\text{In}(\text{OH})_3$, $\text{In}(\text{NO}_3)_3$, InSb , a thallium atom substituted with one or more alkyl groups, TlCl , TlCl_3 , TlBr , TlF , TlF_3 , TlI , Tl_2O_3 , Tl_2S , $\text{Tl}(\text{OH})_3$, $\text{Tl}(\text{NO}_3)_3$, or Tl_3As . Any suitable and effective Group III compound can be employed. Many Group III compound are disclosed in, e.g., *Aldrich Handbook of Fine Chemicals*, 2003-2004 (Milwaukee, WI).

As used herein, "Group III nitride" refers to a compound containing nitrogen covalently bonded to a Group III element. Examples of Group III nitrides include boron nitride (BN), aluminum nitride (AlN), gallium nitride (GaN), indium nitride (InN), and thallium nitride (TlN).

As used herein, "Group III nitride composition" refers to a composition containing a Group III nitride, optionally including other elements, compounds, and dopants.

As used herein, "wetting agent" refers to an element or compound that facilitates the mixing of or a reaction between an otherwise immiscible liquid mixture at the interface of the two components. The wetting agent can be any metal that facilitates interfacial wetting of a binary liquid metal mixture and does not readily react to form covalent bonds with Group III elements. Any suitable and effective wetting agent compound can be employed. Suitable wetting agents include bismuth (Bi), lead (Pb), germanium (Ge), and tin (Sn). Other suitable wetting agents include antimony (Sb), tellurium (Te), and polonium (Po). The reaction mixture can also include a mixture of two or more wetting agents, in any proportion. The reaction mixture can include a wetting agent compound, such as organometallic compounds containing the wetting agent metal or inorganic compounds containing the wetting agent metal. Suitable wetting agent compounds include, e.g., halides, oxides, hydroxides, and nitrates. Many suitable and effective wetting agents and wetting agent compounds are disclosed, e.g., in *Aldrich Handbook of Fine Chemicals*, 2003-2004 (Milwaukee, WI). As used herein, nickel is not a wetting agent.

As used herein, bismuth, germanium, tin, and lead refer to elemental metals, alloys containing these metals, compounds containing these metals, and mixtures thereof.

As used herein, "nitrogen atom source" refers to any substance that can provide a reactive nitrogen atom that forms a chemical bond with a metal.

As used herein, "dopant" refers to a substance that is intentionally added, usually in small amounts, to a pure semiconductor material to alter its conductive properties, typically for use in semiconductors, transistors, and diodes. Suitable dopants include, e.g., beryllium (Be), magnesium (Mg), manganese (Mn), molybdenum (Mo), silicon (Si), and zinc (Zn). Other suitable dopants include rare earth elements, particularly cerium (Ce), samarium (Sm), dysprosium (Dy), erbium (Er), europium (Eu), promethium (Pm), thulium (Tm), and ytterbium (Yb). The dopant can be employed in the form of a pure (elemental) metal. Alternatively, the dopant employed can be in the form of a chemical compound or salt. Rare earth compounds that can be used as dopants, such as, e.g.,

europium chloride (EuCl_3), europium fluoride (EuF_3), europium nitrate ($\text{Eu}(\text{NO}_2)_3$), ytterbium fluoride (YbF_3). Suitable dopants also include, e.g., boron, aluminum, or indium, when the Group III element that is the major component of the reaction mixture is not B, Al, or In, respectively.

As used herein, an “alloy” refers to a homogeneous mixture or solid solution of two or more metals, the atoms of one replacing or occupying interstitial positions between the atoms of another.

As used herein, “shot” refers to essentially circular beads of about 0.5 to about 50 mm in diameter.

As used herein, an “ingot” refers to a bar or block of a metal or an alloy.

As used herein, a “powder” refers to a substance consisting of ground, pulverized, or otherwise finely dispersed solid particles.

As used herein, “monotectic temperature” refers to the fixed temperature at which two immiscible liquids are in equilibrium with a single solid.

As used herein, “consolute temperature” refers to the elevated temperature at which two immiscible liquids become miscible.

As used herein, “substantial decomposition” refers to the Group III nitride decomposing at a faster rate its formation by the reaction of the Group III element with a nitrogen atom source at a given temperature and pressure.

As used herein, an “impurity” refers to a material that is part of a compound or product mixture, of any amount, that is not the same as a recited element or compound.

As used herein, “alkyl” refers to both straight and branched monoradical hydrocarbon that is optionally substituted and optionally saturated; but reference to an individual radical such as “propyl” embraces only the straight chain radical, a branched chain isomer such as “isopropyl” being specifically referred to.

As used herein, “cycloalkyl” refers to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, or cyclooctyl, and substituted versions thereof.

As used herein, “aryl” refers to a phenyl radical, an ortho-fused bicyclic carbocyclic radical having about nine to ten ring atoms in which at least one ring is aromatic, or a heterocyclic radical attached via a ring carbon of a monocyclic aromatic ring containing five or six ring atoms consisting of carbon and one to four heteroatoms each selected from the group consisting of non-peroxide oxygen, sulfur, and N(X) wherein X is absent or is H, O, $(\text{C}_1\text{-C}_8)\text{alkyl}$, phenyl or

benzyl, as well as a radical of an ortho-fused bicyclic heterocycle of about eight to ten ring atoms derived therefrom, particularly a benz-derivative or one derived by fusing a propylene, trimethylene, or tetramethylene diradical thereto.

As used herein, “halo” or “halide” refers to a fluoro, chloro, bromo, or iodo radical.

As used herein, “halogen” refers to either a halide or fluorine, chlorine, bromine, or iodine as diatomic molecules.

As used herein, “reflux temperature” refers to the temperature at which at least one component of a liquid solution is converted into a vapor and is recondensed.

As used herein, “crystalline” refers to the atomic arrangement of a compound having regular arrangement of the atoms in a space lattice.

As used herein, “inert gas” refers to a gas that does not chemically react with the components of the reaction mixture. Examples of inert gases are nitrogen, helium, and argon.

As used herein, “substantially polycrystalline” refers to greater than about 50% of the crystals are of a particular polycrystalline form. Substantially polycrystalline can also refer to greater than 75%, preferably greater than 90%, and more preferably greater than about 95% of the crystals are of a particular polycrystalline form.

Group III elements

Group III nitrides can be prepared by combining a Group III element, a wetting agent, and a nitrogen source to provide a reaction mixture. Typically, the Group III element is first combined with a wetting agent, to provide a first mixture. This first mixture includes a Group III element, wherein the Group III element is boron (B), aluminum (Al), gallium (Ga), indium (In), or thallium (Tl). Preferably, the Group III element is a Row 3, 4, or 5 element, e.g., Al, Ga, or In. More preferably, the Group III element is Ga. The invention also provides that the first mixture can include a mixture of two or more Group III elements, in any suitable and effective proportion.

The Group III element can be in any form convenient for its use in a reaction vessel. Typically the Group III element can be in form of one or more ingots, metal shot, or a powder. Depending on the reaction conditions employed,

the Group III element can also be in one or more physical states, including solid, liquid, and gaseous states.

High purity Group III elements ensures high purity Group III nitrides. The Group III element can be at least about 99% pure by weight. Preferably, the Group III element can be at least about 99.9% pure by weight. More preferably, the Group III element can be about 99.9999% pure by weight.

Wetting agents

An essential component of the preparation of Group III nitrides is a wetting agent. The wetting agent facilitates the mixing of, or miscibility of, two or more otherwise immiscible liquids at their interfaces. A wetting agent will completely wet the exposed surface of a molten Group III element by intruding between a molten Group III element and the gas phase of the reaction mixture. For example, gallium-bismuth alloy wetting is illustrated in FIG. 4. FIG. 4 (a) illustrates a Ga-Bi alloy below $T_{crit} = 262\text{ }^{\circ}\text{C}$, and FIG. 4 (b) illustrates a Ga-Bi alloy above $T_{crit} = 262\text{ }^{\circ}\text{C}$. (Courtesy of H. Tostmann). For a Ga-Bi system (FIG. 4(a)), the high density phase (bismuth) is confined to the bottom of the container when the temperature is lower than the characteristic wetting temperature $T_{crit} = 262\text{ }^{\circ}\text{C}$. Above this critical temperature (FIG. 4(b)), the low surface tension component, bismuth, is present at the interface of the binary mixture. The high density phase completely wets the exposed surface by intruding between the low density phase and the gas phase. Typical wetting agents includes bismuth, germanium, tin, or lead.

In one specific embodiment, the wetting agent does not include bismuth. In another specific embodiment, the wetting agent does not include germanium. In one specific embodiment, the wetting agent does not include tin. In another specific embodiment, the wetting agent does not include lead. In another specific embodiment, the wetting agent does not include a metal salt.

The wetting agent can be in any form convenient for its use in a reaction vessel. Typically the wetting agent can be in the form of a powder, wire mesh, metal shot, or one or more ingots. Depending on the reaction conditions employed, the wetting agent can also be in one or more physical states, including solid, liquid, and gaseous states.

High purity wetting agents ensures high purity Group III nitrides. The wetting agent can be at least about 99% pure by weight. Preferably, the wetting

agent can be at least about 99.9% pure by weight. More preferably, the Group III element can be about 99.999% pure by weight.

Dopants

The reaction mixture can optionally contain dopants. The selection of a particular dopant depends upon the desired characteristics of the Group III nitride composition to be prepared. Dopants are used to alter the conductive properties of an otherwise pure semiconductor, typically for use in semiconductors, transistors, and diodes. The dopant is typically used in less than about 5 weight % of the reaction mixture (Group III nitride and wetting agent), preferably in less than about 2 weight % of the reaction mixture, more preferably in less than about 1 weight % of the reaction mixture.

Reaction Mixtures

Typically the Group III element and the wetting agent are contacted to form a first mixture in a reaction vessel, such as a quartz or boron nitride boat. Alternatively, the Group III element and the wetting agent can be in the form of a metal alloy. It will be appreciated by one skilled in the art that the Group III element – wetting agent alloy can contain other components, such as catalysts or dopants. Any suitable and effective combination can be employed to form the first reaction mixture.

The Group III element and the wetting agent can be employed in any suitable and appropriate amount. The amount of wetting agent employed is dependant upon its effectiveness in wetting the group III metal and facilitating the formation of the Group III nitride. Typically, the wetting agent can be employed in a catalytic (sub-stoichiometric) amount, particularly when bismuth is employed as the wetting agent. The Group III element and the wetting agent can be present in a molar ratio of about 1:1 to about 500:1. Specifically, the Group III element and the wetting agent can be present in a molar ratios of about 2:1, or about 5:1, preferably about 20:1, and more preferably about 100:1, or about 200:1.

The main components of the reaction mixture include the Group III element, the wetting agent, and the nitrogen atom source. The order of mixing can be varied depending on the type of reaction mixture component used. For example, the Group III element can optionally be contacted with a nitrogen atom source prior to contacting the Group III element with the wetting agent.

Alternatively, the wetting agent can be contacted with the nitrogen atom source prior to contacting the wetting agent with the Group III element. In one specific embodiment, borane-ammonia complex ($\text{BH}_3 \cdot \text{NH}_3$) can be used as both the Group III element and a nitrogen atom source. It should be noted that more than one specific nitrogen atom source can be used in any given embodiment.

Different methods of contacting the nitrogen source with the Group III element can be employed. Typically, a nitrogen atom source gas is passed over a heated mixture of the Group III element and the wetting agent. The mixture of the Group III element and the wetting agent can be contacted with the nitrogen atom source on the surface of the mixture. Alternatively, the nitrogen atom source can be contacted with the mixture at the interior of the mixture, for example, by forcing a gaseous nitrogen atom source into a liquid mixture of the Group III element and the wetting agent.

Purging

The Group III element and wetting agent are typically placed in a quartz, boron nitride, silicon carbide, or tantalum carbide reaction vessel. The vessel is typically either a furnace, or is contained in a furnace. Purging the reaction vessel with a flowing a gas allows for the removal of substances that can form impurities in the Group III nitride, particularly water and oxygen. Gases used for purging can be purified before purging the reaction vessel. Purification of the purge gas includes removing oxygen, water vapor, and other impurities. The reaction vessel is typically purged with hydrogen or an inert gas. Gases used for purging include, e.g., hydrogen, helium, argon, and nitrogen, or any combination thereof. For example, purging can be performed using hydrogen gas, either alone, or in combination with an inert gas. Heating a Group III metal under flowing hydrogen gas can help reduce any remaining trace amounts of Group III metal oxide on the metal surface.

The vessel is preferably purged until oxygen has been completely removed from the reaction vessel, chamber, or furnace. Purging the reaction vessel can be facilitated by first evacuating a sealed vessel to reduce its internal pressure before flowing the purge gas through the vessel. Generally, the purging can occur at any time and at any temperature before a nitrogen atom source is added. The Group III element and wetting agent are typically in a vessel that is purged by a flowing gas and is heated at the same time. The vessel can be

purged for at least 10 minutes. Preferably, the vessel is purged for about 1-4 hours. Specifically, the vessel can be purged for about 1.5 hours.

Nitrogen atom source

The nitrogen atom source provides the nitrogen atom that becomes the reactive nitrogen species, which in turn reacts with the Group III element to form the Group III nitride. The nitrogen atom source can be a gas, liquid, or a solid. One specific nitrogen atom source is ammonia, initially added as either a liquid or a gas. Alternatively, the ammonia can be in the form of a complex or a salt. Any nitrogen atom source can be treated to remove impurities. For example, when ammonia gas is used as a nitrogen atom source, an ammonia purifier can be used to remove residual water vapor and oxygen (impurities).

Ammonia is a preferred nitrogen atom source, but other nitrogen atom source can be employed. The nitrogen source can be an amine substituted with one or more alkyl, cycloalkyl, or aryl groups. The nitrogen atom source can also be an ammonium salt, for example, an ammonium halide. Specific ammonium halides include ammonium fluoride, ammonium chloride, ammonium bromide, and ammonium iodide. The nitrogen atom source can also be ammonium hydroxide, hydrazine, or lithium nitride (Li_3N). Other alkali metal nitrides can also be used, such as sodium nitride, or potassium nitride. The nitrogen atom source can also include nitrogen-containing organometallic compounds or nitrogen-containing inorganic compounds. The nitrogen atom source can further be an alkali metal azide, e.g., lithium azide, sodium azide, or potassium azide.

The nitrogen atom source can produced by discharge of an electric arc through liquid nitrogen, or alternatively, gaseous nitrogen. As such, a nitrogen atom source can be produced as disclosed by Anders (A. Anders and S. Anders, *Plasma Sources Sci. Technol.* **1995**, 4, 571). An arc discharge method can also be used to otherwise facilitate the production of the Group III nitride in the reaction mixture.

A liquid or gaseous nitrogen atom source can be passed over or through the reaction mixture. Various rates of passage over or though the mixture can be employed. One gas flow rate can be about 100-900 standard cubic centimeters per minute (sccm), or more preferably about 200-800 sccm. Specific flow rate can be about 400 sccm, about 500 sccm, or about 600 sccm.

Temperature and duration parameters

Heating the reaction mixture provides the energy required to convert solid reactants into liquids or gases, and to convert the reactants into products, e.g. Group III nitrides. Typically the mixture of the Group III element and the wetting agent are formed into a melt before the nitrogen atom source is added. For efficient conversion of the reaction mixture to a Group III nitride composition, the reaction must typically be heated to at least the monotectic temperature, and preferably, to at least the consolute temperature. Specifically, the mixture can be heated to at least about 262 °C before the nitrogen atom source is added. More specifically, the mixture can be heated to at least about 650 °C before the nitrogen atom source is added.

After the Group III element and wetting agent are contacted with the nitrogen atom source, the temperature is typically increased to a higher temperature. Specifically, the mixture can be heated to at least about 500 °C. More specifically, the mixture can be heated to at least about 900 °C, or alternatively to about 1000 °C.

In certain embodiments, the mixture can be heated to a temperature less than that which causes substantial decomposition of the Group III nitride. For the preparation of GaN and InN compositions, one maximum temperature of the reaction is 1250 °C. For the preparation of AlN compositions, one maximum temperature of the reaction is 1500 °C. It will be appreciated by one skilled in the art that each Group III nitride composition possesses a temperature at which the nitride begins to decompose. Thus, to maintain high purity of the Group III nitrides produced, the reaction temperature should not be heated to a temperature higher than the decomposition temperature of the Group III nitride. For certain reaction components, the mixture can be heated to no greater than about 1100 °C before the nitrogen atom source is added, or alternatively about 1500 °C. For other reaction components, the mixture can be heated up to about 2200 °C before the nitrogen atom source is added.

Various reaction mixtures require different durations to reach completion. The reaction mixture can be heated for at least 30 minutes after the mixture is contacted with the nitrogen atom source. Also, the mixture can be heated for about 1-20 hours, or more preferably for about 3-8 hours. In one specific embodiment, the mixture is for about 5 hours. The mixture can also be

heated for up to about ten days. See for example, FIG. 3, which illustrates the yields of GaN powder plotted against reaction time in NH_3 at 1000 °C with 5 weight % Bi as the wetting agent.

Group III nitride composition

High purity Group III nitride can be prepared by the methods disclosed herein. The Group III nitride composition can be produced in greater than about 50% purity by weight. The Group III nitride composition can also be produced in greater than about 75% purity by weight. Typically, the Group III nitride composition is produced in greater than about 95% purity by weight. Preferably, the Group III nitride composition is produced in greater than about 99% purity by weight. More preferably, the Group III nitride composition is produced in greater than about 99.9% purity by weight. The percent purity by weight can readily be determined by those of skill in the art by glow discharge mass spectrometry (GDMS).

The Group III nitride composition formed can include two or more Group III nitrides. For example, GaN forms a continuous range of solid solutions with AlN and InN, separately or together. These combinations can be represented by, e.g., the following formulae: $\text{Ga}_x\text{Al}_{(1-x)}\text{N}$, $\text{Ga}_x\text{In}_{(1-x)}\text{N}$, and $\text{Ga}_x\text{Al}_y\text{In}_{(1-x-y)}\text{N}$. The various combinations need not include gallium. The amount of substitution is determined by the properties desired in the resulting composition.

The Group III nitride composition can be further purified after the initial reaction is complete, for example by removing excess wetting agent from the Group III nitride formed. After this purification step, the Group III-nitride composition can be produced in greater than about 99% purity by weight, more preferably in greater than about 99.5% purity by weight. In certain embodiments, the Group III-nitride composition can be produced in greater than about 99.9% purity by weight. FIG. 7 illustrates a typical Cathodoluminescence (CL) spectrum of synthesized GaN powder at room temperature. FIG. 8 shows Raman spectroscopy of (a) commercial GaN powder vs. (b) synthesized GaN powder at room temperature. The GDMS results for a commercial powder and a GaN powder produced by the disclosed methods are both presented in Table 1 in the Examples section, below.

The powder produced by the methods described is typically crystalline. Specifically, the Group III nitride composition can be substantially hexagonal polycrystalline. Alternatively, the Group III nitride composition can be substantially cubic polycrystalline. FIG. 5 illustrates a typical XRD pattern, using Cu K_{α} radiation, of GaN powder produced by the disclosed procedures after removal of a Bi wetting agent. A typical $\theta-2\theta$ scan mode XRD pattern of the powder after the removal of Bi is illustrated in FIG. 5. The pattern corresponds well with that of hexagonal GaN reported in the ASTM X-ray powder data file. This GaN powder clearly shows a strong (0001) orientation because (0002) is the strongest observed peak.

The powder formed from the Group III nitride composition can form crystalline plates. In one embodiment, the diameter of the plates can be about 0.1 to about 50 μm . The powder can also be plates of about 1 to about 20 μm in diameter. The Group III-nitride composition produced can form single crystals. FIG. 6 (a) illustrates a scanning electron microscopy (SEM) image of synthesized GaN powder, showing a 10 μm resolution bar. FIG. 6 (b) illustrates a SEM image of a large GaN plate, showing a 2 μm resolution bar.

Pressure

Altering the atmospheric pressure of the reaction mixture can change the temperature and duration required to produce the Group III nitrides compositions. The method can be conducted at pressures of less than one atmosphere. Specifically, the method can be conducted at pressures as low as about 10 Torr. Alternatively, the method can be conducted at pressures of greater than one atmosphere. Specifically, the method can be conducted at pressures as high as about 10,000 Torr. It will be appreciated by the skilled artisan that specific pressures between about 10 Torr and about 10,000 Torr can also be employed. Certain specific pressures include any of about 2, 4, 6, 8, or 10 atmospheres. Lower reaction temperatures can optionally be employed when the reaction is conducted under pressure (e.g., about 550 $^{\circ}\text{C}$). Also, higher temperatures can optionally be employed when the reaction is conducted under reduced pressures.

The Group III nitride composition is typically produced in extremely high purity, as determined by Glow Discharge Mass Spectrometry (GDMS) and X-Ray Diffraction (XRD) analysis. Various methods can be employed to further

increase the purity by removing the wetting agent. The Group III nitride composition formed by the methods disclosed herein is typically cooled to ambient temperature before further purification, but cooling is not always required.

For convenient handling of the Group III nitride, the composition is typically formed into a powder. The powder formation process can be performed under a suitably inert atmosphere to prevent oxidation or hydration of sensitive substrates. The Group III nitride composition can be formed into a powder by crushing, for example, using a mortar and pestle. The skilled artisan will appreciate that powders of various grain sizes can be readily prepared. A powder can be formed into particles as small as about one micron in diameter. The Group III nitride can also be formed into a powder, wherein the powder includes ultrafine particles, e.g., particles of less than about 0.1 μm in diameter. Ultrafine particles are important because such particles typically possess optical and mechanical properties different than those of the corresponding bulk materials.

Purification techniques

I. Evaporation

One method of purifying the Group III nitride composition powder formed is by heating under a flowing gas to remove the wetting agent after the reaction process. Specifically, the powder can be heated under ammonia gas. Typically, the Group III nitride composition powder can be heated to at least about 800 °C. Specifically, the Group III nitride composition powder can be heated to at least about 1000 °C. In one specific embodiment, the Group III nitride composition powder can be heated to about 1030 °C. Alternatively, the Group III nitride composition powder can be heated to up to about 1500 °C. For the preparation of a GaN composition, the GaN composition powder can be heated up to about 1250 °C.

The duration of heating can influence the level of purity. In one embodiment, the Group III nitride composition powder is heated for at least 30 minutes under a gas. In another embodiment, the Group III nitride composition powder is heated for about 5 hours under a gas, for example, ammonia gas.

II. Oxidative purification

One alternative means of purifying the Group III nitride powder is by contacting the powder with a solvent or solvent system, oxidizing the wetting agent to form a soluble compound, followed by removing the soluble oxidized wetting agent. For example, the Group III nitride composition powder can be contacted with one or more solvents and one or more oxidants to form a solution of the oxidized wetting agent, followed by physically separating oxidized wetting agent from the solid Group III nitride powder.

The solvent or solvents preferably dissolve the oxidized wetting agent. The solvent or solvents used to dissolve the wetting agent include an alkyl, cycloalkyl, or aryl, optionally substituted with one or more polar groups, wherein the alkyl or cycloalkyl is optionally partially unsaturated, and wherein the alkyl or cycloalkyl is optionally interrupted with one or more oxy, amino, or thio groups. Examples of polar groups are, e.g., hydroxyl, amino, thio, and halo substituents. In one specific embodiment, one solvent can be ethanol.

The oxidant can be a halogen, or alternatively, any suitable and effective oxidizing agent. Specifically, the oxidant can be iodine.

Elevated temperatures can be employed to facilitate the dissolution of the oxidized wetting agent. The first solution can be heated under refluxing conditions, e.g., about one hour to about two days. Preferably, the first solution can be heated for about one day. The separation of the Group III nitride and the oxidized wetting agent can be achieved by filtration.

The powder can be dried to remove any remaining solvent or solvents. Preferably, the powder is dried to remove all recognizable traces of the solvents, for example, as analyzed by GDMS. Further removal of remaining oxidant from the Group III nitride composition can also be performed, as necessary.

III. Dissolution

The Group III nitride composition can be purified by dissolving unreacted Group III metals and wetting agents in an acid. Specifically, the acid can be hydrochloric acid, or a nitric acid / hydrofluoric acid combination. Alternatively, a mixture of hydrochloric acid and hydrogen peroxide solution can be used. Each technique can be followed by aqueous rinses and drying.

Reaction apparatus

The vessel used for producing the Group III nitride composition can be a furnace, or optionally be a vessel contained in a furnace. FIG. 1 illustrates a

schematic view of a vertical furnace used for preparing Group III nitrides. FIG. 2 illustrates a schematic view of a horizontal furnace used for preparing Group III nitrides. The vessel containing the Group III nitride and the wetting agent mixture can be a quartz vessel. Alternatively, the vessel can be made of, or is lined with, boron nitride, graphite, SiC coated graphite, TaC coated graphite, molybdenum, tungsten, or TaC.

The reaction mixture can be agitated to facilitate mixing. Agitation can be achieved by stirring or shaking. Agitation or mixing can also be performed by other methods, such as through microwave irradiation or by producing a centripetal or centrifugal force upon the reaction mixture.

Additional methods

The method of making Group III nitrides disclosed herein can include various optional steps. For example, the invention provides a method for making a Group III nitride composition, the method comprising: (a) heating a first mixture comprising a Group III element or a compound containing a Group III element, and one or more wetting agents selected from the group of bismuth, germanium, tin, and lead, or a compound thereof, in any combination, to a temperature and for a period of time, sufficient to liquefy at least a portion of the Group III element, thereby providing a second mixture; (b) contacting the second mixture with a nitrogen atom source to provide a third mixture; and (c) heating the third mixture to a temperature and for a period of time, sufficient to form a Group III-nitride composition.

In another embodiment, the invention provides a method for making a Group III nitride composition, the method comprising: (a) contacting a Group III element or compound and a wetting agent to provide a first mixture; (b) heating the first mixture to a temperature that changes at least some of the first mixture to a liquid state to provide a second mixture; (c) contacting the second mixture with a nitrogen atom source; (d) heating the second mixture and the nitrogen atom source up to about 1500 °C for a sufficient amount of time to form a Group III nitride composition.

The invention also provides a method for making a Group III nitride composition, the method comprising: (a) contacting a Group III element or compound and a wetting agent to provide a first mixture; (b) heating the first mixture to about 650 °C; (c) contacting the first mixture with a nitrogen atom

source; (d) heating the first mixture and the nitrogen atom source up to about 1000 °C for a sufficient amount of time to form a second mixture; (e) allowing the second mixture to cool; (f) forming the second mixture into a powder; and (g) heating the powder under ammonia for a time and temperature sufficient to evaporate at least a portion of the wetting agent or any other impurity removable by such method.

The methods described herein can be employed for the preparation of other Group III – Group V compounds, such as Group III phosphides, arsenides, and antimonides, by using an appropriate and suitable Group V atom source in place of the nitrogen atom source. Furthermore, the process can also be used for the preparation of transition metal nitrides and rare earth element nitrides, by using suitable and effective transition metals or rare earth elements in place of the Group III elements. For example, titanium, vanadium, chromium, niobium, and tantalum nitrides can be prepared by replacing the Group III element with the appropriate transition metal or rare earth element, and following the method for preparing Group III nitrides, and alternatively, phosphides, arsenides, and antimonides.

Examples

Example 1: General Gallium Nitride Preparation Methods

Methods and Materials:

The starting materials used were 99.9999% pure gallium shot from Eagle-Picher Technologies, LLC. , 99.999% bismuth shot from Spex Industries, and 99.9999% ammonia from Airgas Inc. An ammonia purifier was used to remove residual water vapor and oxygen from the NH₃ gas. Twenty-five grams of Ga shot was mixed with varying mole fractions of Bi in a quartz tube 5 cm in diameter and 25 cm deep. Because the Ga was added as a solid piece, Bi was distributed above and below it to ensure rapid mixing upon melting. The quartz tube was loaded into a vertical furnace. A schematic view of the system is illustrated in FIG. 1. A matrix of temperatures (900-1050 °C), NH₃ flow rates (200-800 sccm), Bi concentrations (0-20% mole fraction) and reaction times (3-6 hours) was investigated to optimize the synthesis.

After purging the tube with N₂ for 1 hour, the sample was heated under flowing N₂. When the melt temperature reached 650 °C, the gas was switched from N₂ to NH₃, and then the furnace was heated in one hour to the desired

reaction temperature. After the reaction, the sample was allowed to cool to room temperature under flowing NH_3 . The material was removed from the boats, crushed and slightly ground with a mortar and pestle. Twenty-five grams of metal Ga were fully converted into approximately 30 grams of high purity GaN (> 99% yield) within 3-6 hours. The Bi was easily removed after powder formation by one of the two purification methods discussed below. No further purification of the powder was necessary. In one embodiment of the invention, the optimum conditions for the complete conversion of the Ga into GaN were a reaction temperature of 1000 °C, 500 sccm NH_3 flow, 0.5% mole fraction Bi, and 5 hours reaction time. Higher Bi concentrations also resulted in complete conversion to GaN under similar conditions, but minimal Bi content is desired to produce the highest purity material.

Results and Analysis:

I. Without a wetting agent:

Initial experiments used pure gallium metal as the reactant with no Bi added. Even after 24 hours of reaction with NH_3 at 1000 °C, only a thin GaN crust was formed on the surface of the melt. The yield of GaN powder was estimated to be lower than 1% after removing the large excess of Ga via etching with hydrochloric acid.

At first, it was suspected that the low yield might have resulted from the metal Ga poorly wetting the surface of the quartz tube. Thus, the surface was roughened to improve the wetting of metal Ga inside the quartz tube. However, liquid metal Ga was still confined by the thin GaN layer. The GaN crust over the molten Ga appeared to be continuous with no visible cracks or holes, apparently preventing NH_3 from reaching the Ga below. Because the crust inhibited further GaN production, the diffusion of Ga or N through the solid GaN in the crust must be very slow at these temperatures.

II. With a Bi wetting agent

Several candidate metals were screened to find the best potential catalyst for Ga conversion: Bi, Ge, Sn and Pb. For both Ga-50%Sn and Ga-50%Pb, only a thin GaN crust was produced on top of the molten alloy. The gallium in both the Ga-50% Ge and Ga-50% Bi alloys had almost completely reacted at 900 °C under flowing NH_3 . However, with only a 10% molar fraction of Ge, the metal

Ga was only partially converted into GaN, while with 10% Bi, the metal Ga reacted completely. Thus, Bi was selected as the catalyst for further study.

The Bi ratio, temperature, NH₃ flow and reaction time were varied to determine the optimum conditions to synthesize the GaN powder. In marked contrast to the experiments with pure Ga, all the gallium reacted completely with NH₃ at 900-1050 °C within 3-6 hours. With a high ratio of Bi in the alloy (>5%), Ga was fully converted into GaN throughout the temperature range 900-1050 °C, within 3 hours. The production of GaN from Ga-5%Bi alloys for reaction times from 1 hour to 1 week was explored at 900 °C. The dependence of yield of GaN on reaction time is shown in FIG. 3. Surprisingly, most of the Ga was converted to GaN in only one hour after reaching 900 °C. The powder was gray to dark gray because of the remaining Bi. The powder color became progressively lighter as the Bi concentration was decreased. The particle shape and size varied with different Bi concentrations. Needle-like crystals were common at high Bi concentrations, while plate-like particles predominated at low Bi concentrations. One set of optimum conditions are 0.5% Bi, 1000 °C, 500 sccm NH₃ flow and 5 hours reaction. The powder produced was off-white to light gray. This material was selected for further detailed characterization.

For the Ga-Bi system, the high density phase (Bi) is confined to the bottom of the container when the temperature is lower than the characteristic wetting temperature $T_{crit} = 262$ °C; see FIG. 4(a). Above this critical temperature, the low surface tension component, Bi, is present at the interface of the binary mixture. The high density phase completely wets the exposed surface by intruding between the low density phase and the gas phase; see FIG. 4(b). Even in Ga-rich alloys of Ga-Bi, Bi is highly concentrated on the surface of the Ga-rich liquid to form a film that is at least 30Å thick at temperatures higher than 262 °C (Tostmann, et al. *Phys. Rev. Lett.* **2000**, *84*, 4385). This Bi layer apparently prevents GaN crust formation and facilitates the full, rapid conversion from Ga to GaN.

III. Removal of Bi (Purification Processes):

To remove the residual Bi from the GaN powder, two methods have been developed. The first method is an overnight reflux of the powder with iodine in ethanol. The bismuth iodide is then removed from the mixture by vacuum filtration.

An alternate, and potentially more efficient, method of Bi removal is to heat the powder to 1030 °C under flowing NH₃ gas for 5 hours. At this temperature, the Bi equilibrium vapor pressure is about 1200 Pa, more than 1000 times greater than that of Ga, a mere 1 Pa. Bi was easily removed by evaporation while the NH₃ passed over the mixture prevented GaN from decomposing. The powder color was lighter after this annealing process, and the small Bi peak in the powder XRD pattern disappeared.

IV. Characterization:

The crystalline quality of the GaN powder was characterized by using a Scintag XDS 2000 powder X-ray diffractometer with a 1.8 kW sealed copper X-ray source. The surface morphology of the GaN powder was observed by scanning electron microscopy (SEM). Cathodoluminescence was performed as an additional screen of purity. Raman spectroscopy was carried out at room temperature. GDMS was used by Shiva Technologies Inc. to analyze the purity of the GaN powder.

- *X-ray Diffraction:* The GaN powder synthesized via the reaction of Ga and NH₃ with the Bi catalyst was examined by XRD using Cu K_α radiation. Once the Bi was removed, only GaN peaks were observed in the pattern. No free Ga or other phases were detected. Figure 5 demonstrates a typical $\theta - 2\theta$ scan mode XRD pattern of the powder after the removal of Bi. The pattern corresponds well with that of hexagonal GaN reported in the ASTM X-ray powder data file. The GaN powder clearly has a strong (0001) orientation because (0002) is the strongest observed peak.
- *Scanning electron microscopy:* Figure 6(a) shows an SEM image of GaN powder grown under optimum conditions. The particle size distribution was 1-10 μm , with a majority of the particles around 2 μm . While several particle morphologies were observed (plates, polyhedra, and needles), the predominant shapes were plates, corresponding to the XRD result with (0002) as the highest peak. Some GaN plates are very large, more than 20 μm in diameter and 5 μm thick; see FIG. 6(b). The mechanism for this preferential plate growth is under investigation.
- *Cathodoluminescence:* The optical properties of GaN powder synthesized by this method were investigated using cathodoluminescence at room temperature. Typical commercial powder was characterized at the same

conditions for comparison. The excitation source was a 5 KeV electron gun focused to a 5 mm diameter spot. Figure 7 is CL spectrums measured at room temperature for GaN powder synthesized by a procedure of this invention and typical commercial powder. The spectrum of our powder showed a strong band edge emission at 3.46eV without a deep level yellow emission. The luminescence at 3.46 eV measured at room temperature has a full width at half maximum (FWHM) of approximately 50 meV. Typical commercial powder showed much less intensity compared to our powder. For easy comparison, the intensity of commercial powder has been amplified by 100 times in the figure. Clearly, the intensity of our powder is 500 times larger than the commercial powder at the same measure conditions. This excellent luminescence property of our powder indicates the growth of high crystalline GaN.

- *Raman Spectroscopy:* Raman scattering measurements were carried out at room temperature using a triple monochromator Raman system equipped with a charge coupled detector. An Ar⁺ laser ($\lambda = 514.5$ nm) was used as the source of excitation. The typical laser spot size was 1 μm and the spectral resolution was approximately 2.5 cm^{-1} . The power on the sample was 50 mW. Figure 8 (a) and (b) show the Raman spectra of the typical commercial powder and the GaN powder made through the processes of this invention.

The Raman spectrum of the synthesized GaN powder was consistent with other reports in the literature (E. V. Konenkova, Y. V. Zhilyaev, V. A. Fedirko, D. R. T. Zahn, *Appl. Phys. Lett.* **2003**, 83, 629; F. A. Ponce, J. W. Steeds, C. D. Dyer, G. D. Pitt, *Appl. Phys. Lett.* **1996**, 69, 2650; B. J. Skromme, K. C. Palle, C. D. Poweleit, H. Yamane, M. Aoki, F. J. DiSalvo, *Appl. Phys. Lett.* **2002**, 81, 3765; V. Yu. Davydov, Yu. E. Kitaev, I. N. Goncharuk, et. al, *Phys. Rev. B.* **1998**, 58, 12,899). It corresponded to the following classifications and frequencies: E2 (low) at 142 cm^{-1} , A1 (TO) at 532 cm^{-1} , E1 (TO) at 558 cm^{-1} , E2 (high) at 567 cm^{-1} , A1 (LO) at 733 cm^{-1} . The Raman signals from the commercial powder were weak and only E2 (high) and A1 (LO) peaks appeared clearly there. Therefore, this indicates a much better quality of GaN powder produced through the method reported here, compared to commercial GaN powder.

- *Glow Discharge Mass Spectrometry:* Glow discharge mass spectrometry (GDMS) is an extremely powerful tool for performing trace and ultra-trace

elemental analysis on inorganic solid materials. As a direct solid sampling technique it is capable of reaching detection limits far below most other analytical techniques. Typical commercial powder and our powder were analyzed by GDMS by Shiva Technologies Inc. The GDMS results for both commercial powder and powder produced by the disclosed methods are presented in Table 1.

Element	Concentration [ppm wt. %]	Concentration [ppm wt. %]	Element	Concentration [ppm wt. %]
B	3.3	5.2	Zn	0.12
C	~ 50	- *	Br	< 0.1
O	~ 650	- *	Zr	0.12
Na	1.3	2.5	Mo	< 0.05
Mg	0.83	5.6	Rh	< 0.05
Al	210	19	Ta	< 100
Si	380	58	W	< 0.05
P	0.42	1.5	Bi	420
S	2.1	180	Pt	< 0.05
Cl	11	78	Pb	< 0.05
K	4.1	< 0.05	Sn	< 0.05
Ca	0.58	2.6	Sb	< 0.05
Ti	3.7	0.16	Te	< 0.05
Cr	1.2	0.71	I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Re, Os, Ir, Tl, Sc, Sr, Y, Nb	< 0.05
Mn	0.07	< 0.01		
Fe	8.3	4.6		
Co	< 0.01	0.16	Ge, As, Se, Rb, V, Ru, Au, Hg, Ag, Cd, Li	< 0.1
Ni	0.5	0.91		
Cu	0.07	16		

- “-” indicates that the concentration of the element exceeded the measurement range of the GDMS, typically greater than 3-5%. Indium concentration is not shown in the table because it was present in the binder material.

The typical commercial powder contained oxygen and carbon impurity concentrations above the measurement limits of GDMS, indicating that each constituted more than 3-5% by weight. It is clear that the carbon and oxygen levels were decreased dramatically in the synthesized GaN powder. The relatively higher Al and Si concentrations in our GaN powder results from the quartz tube used in the experiments. The high Bi concentration reflected the fact that the Bi removal process was not performed in this test sample. However, this Bi could be efficiently eliminated by the evaporation process discussed previously.

Based on the GDMS analysis, the overall purity of the typical commercial powder was worse than 94% (at least 3% oxygen and 3% carbon). However, the GaN powder made through the method disclosed herein could achieve 99.9% and even 99.99% purity if Bi was removed and Al and Si contamination from quartz were avoided by using a boron nitride (BN) boat. To current knowledge, the GaN powder produced by this disclosed procedure possesses a higher purity than any previously reported in the literature.

Discussion:

Gram-scale quantities of GaN powder were synthesized reproducibly by adding Bi as a catalyst. One hundred grams of gallium metal has been successfully converted into 120 grams of high-purity GaN powder. Larger scales can be achieved with larger quartz tubes and furnace sizes.

The Bi catalyst was very effective at increasing the growth rate of GaN powder. This is an economically viable process to produce high purity, single phase, and highly luminescent GaN powder. One set of optimal synthetic conditions are: 0.5% mole fraction of Bi, 1000 °C, 500 sccm NH₃ flow and 5 hours reaction time. The powder was characterized by XRD and identified as hexagonal GaN. SEM images revealed the powder consisted of fine crystals of 1-10 μm. The CL spectrum was also measured at room temperature and only a strong band-edge emission of GaN was observed. The results from GDMS analyses indicated very high purity GaN powder. The synthesized material is to be used as the source material for the growth of bulk crystals using sublimation. Given its excellent luminescence, this GaN powder could also be used in organic LEDs.

Example 2: Specific Gallium Nitride Preparation, Purification #1

Twenty-five grams 99.9999% pure Ga shot was mixed with 0.5% mole fraction 99.999% pure Bi in a quartz tube (5 cm in diameter and 25 cm deep). The Ga was added as a solid piece, and Bi was distributed above and below it to ensure rapid mixing upon melting. The quartz tube was loaded into a vertical furnace similar to that illustrated by the schematic in FIG. 1.

After purging the tube with N₂ for 1 hour, the sample was heated under flowing high purity N₂. When the melt temperature reached 650 °C, the gas was switched from N₂ to 99.9999% pure NH₃ gas at a flow rate of 500 sccm. An ammonia purifier was used prior to NH₃ addition to remove residual water vapor and oxygen from the NH₃ gas. The furnace was then heated in one hour to 1000 °C. After five hours, the sample was allowed to cool to room temperature under flowing NH₃. The material was removed from the boats, crushed and slightly ground with a mortar and pestle.

Twenty-five grams of metal Ga were fully converted into approximately 30 grams of high purity GaN (> 99% yield) in five hours. The remaining Bi was easily removed after powder formation by heating the powder to 1030 °C under flowing NH₃ gas for 5 hours. The powder color was lighter after this annealing process, and the small Bi peak in the powder XRD pattern disappeared.

Example 3: Specific Gallium Nitride Preparation, Purification #2

Twenty-five grams 99.9999% pure Ga shot was mixed with 0.5% mole fraction 99.999% pure Bi in a quartz tube (5 cm in diameter and 25 cm deep). The Ga was added as a solid piece, and Bi was distributed above and below it to ensure rapid mixing upon melting. The quartz tube was loaded into a vertical furnace similar to that illustrated by the schematic in FIG. 1.

After purging the tube with N₂ for 1 hour, the sample was heated under flowing high purity N₂. When the melt temperature reached 650 °C, the gas was switched from N₂ to 99.9999% pure NH₃ gas at a flow rate of 500 sccm. An ammonia purifier was used prior to NH₃ addition to remove residual water vapor

and oxygen from the NH_3 gas. The furnace was then heated in one hour to 1000 °C. After five hours, the sample was allowed to cool to room temperature under flowing NH_3 . The material was removed from the boats, crushed and slightly ground with a mortar and pestle.

Twenty-five grams of metal Ga were fully converted into approximately 30 grams of high purity GaN (> 99% yield) in five hours. The remaining Bi was easily removed after powder formation by an overnight reflux of the powder with iodine in ethanol. The bismuth iodide was then removed from the solution by vacuum filtration.

Example 4: Gallium Nitride Prepared in a Boron Nitride Boat

In this example, a BN boat was used as the reaction vessel. The method of Example 2 was used, except where noted below. The reactants were metal gallium (25g), bismuth (0.757g (1 mol%)), and purified ammonia gas. The reaction temperature was 1000 °C, the reaction time was 4 hours, and the NH_3 flow rate was 600sccm.

Results: Metal Ga was fully converted into GaN powder within 4 hours. The color of the powder produced was light gray. Twenty-five grams of metal gallium was fully converted into 30.735 g of GaN powder. The GaN powder was analyzed by XRD and GDMS; XRD analysis confirmed that the powder was composed of only GaN single phase. FIG. 9 illustrates the XRD plot for the GaN powder produced in BN boat after removal of the bismuth wetting agent by evaporation. GDMS indicated that the purity of the powder was greater than 99.91%. Table 2 illustrates a comparison of the GaN purity of Example 2 and Example 4, as analyzed by GDMS.

Table 2. A comparison of the GaN purity of Example 2 and Example 4, as analyzed by GDMS. (Analysis by Shiva Technologies, Inc.)

Element	Example 2 Conc. [ppm wt]	Example 4 Conc. [ppm wt]	Element	Example 2 Conc. [ppm wt]	Example 4 Conc. [ppm wt]
Li	0.02	< 0.01	Pd	< 0.5	< 0.5
Be	< 0.01	< 0.01	Ag	< 0.1	< 0.1
B	3.3	60	Cd	< 0.1	< 0.1
C	~ 50	~8	In	Binder	Binder
N	Matrix	Matrix	Sn	< 0.05	< 0.05
O	~ 650	~450	Sb	< 0.05	< 0.05
F	< 0.5	< 0.5	Te	< 0.05	< 0.05
Na	1.3	1.6	I	< 0.05	< 0.05
Mg	0.83	<0.05	Cs	< 0.05	< 0.05
Al	210	0.16	Ba	< 0.05	< 0.05
Si	380	46	La	< 0.05	< 0.05
P	0.42	<0.05	Ce	< 0.05	< 0.05
S	2.1	39	Pr	< 0.05	< 0.05
Cl	11	12	Nd	< 0.05	< 0.05
K	4.1	< 0.05	Sm	< 0.05	< 0.05
Ca	0.58	0.17	Eu	< 0.05	< 0.05
Sc	< 0.05	< 0.05	Gd	< 0.05	< 0.05
Ti	3.7	0.02	Tb	< 0.05	< 0.05
V	< 0.1	< 0.1	Dy	< 0.05	< 0.05
Cr	1.2	18	Ho	< 0.05	< 0.05
Mn	0.07	0.58	Er	< 0.05	< 0.05
Fe	8.3	2.8	Tm	< 0.05	< 0.05
Co	< 0.01	<0.01	Yb	< 0.05	< 0.05
Ni	0.5	4.1	Lu	< 0.05	< 0.05
Cu	0.07	0.25	Hf	< 0.05	< 0.05
Zn	0.12	0.33	Ta	< 100	<100
Ga	Matrix	Matrix	W	< 0.05	< 0.05
Ge	< 0.1	< 0.1	Re	< 0.05	< 0.05
As	< 0.1	< 0.1	Os	< 0.05	< 0.05
Se	< 0.1	0.22	Ir	< 0.05	< 0.05
Br	< 0.1	<0.1	Pt	< 0.05	< 0.05
Rb	< 0.1	< 0.1	Au	< 0.1	< 0.1
Sr	< 0.05	< 0.05	Hg	< 0.1	< 0.1
Y	< 0.05	< 0.05	Tl	< 0.05	< 0.05
Zr	0.12	< 0.05	Pb	< 0.05	< 0.05
Nb	< 0.05	< 0.05	Bi	420	15
Mo	< 0.05	<0.05	Th	< 0.01	< 0.01
Ru	< 0.1	< 0.1	U	< 0.01	< 0.01
Rh	< 0.05	<0.05			

The GaN powder of Example 2 was synthesized in quartz vessel. The GaN powder of Example 4 was synthesized in the BN boat. As shown in Table 2, the Si and Al concentrations were dramatically reduced when a BN boat was used as a reaction vessel. The purity in of Example 4 is at least 99.91%. The purity can be further improved by the use of SiC or TaC coated boats in place of quartz or BN reaction vessels.

Example 5: Gallium Nitride Doped with 0.5 mol% Erbium

In this example, Erbium was added to the reaction mixture to produce an Erbium-doped GaN powder. The method of Example 2 was used, except where noted below. The reactants were metal gallium (25g), bismuth (0.757g (1 mol%)), erbium (Er) (0.305g (0.5 mol%)), and purified ammonia gas. The reaction temperature was 1000 °C, the reaction time was 5 hours, and the NH₃ flow rate was 600sccm. A quartz reaction vessel was used to contain initial reactants.

The Ga-Er-Bi alloy was prepared as follows. Er was formed into small particles in a glove box under an Ar atmosphere. The metal reactants (Ga, Er and Bi) were transferred into a small quartz tube and the tube was sealed to maintain an Ar atmosphere and the quartz tube and contents were placed in a furnace. The temperature was gradually increased to 350-400°C as the furnace was purges with Ar gas. The quartz tube was agitated through vibration to facilitate mixing and alloy formation. The metals were heated for 1-2 hours to ensure a uniform and homogeneous alloy was formed in the quartz tube. The alloy was transferred a reaction vessel in a glove box and was sealed. Care is taken at all times to prevent exposure of the Er with nitrogen and oxygen gases.

Results: the Ga-Er-Bi alloy was fully converted into a GaN doped with Er powder within 5 hours. The color of the powder formed was light gray, and weighted 30.025 grams. XRD analysis was performed, confirming GaN formation.

Example 6: Gallium Nitride Doped with 0.25 mol% Erbium

The method of Example 5 was used, but the quantity of erbium was changed to 0.25 mol% (0.152 g). High conversion rates were observed, but some product

adhered to the reaction boat, contributing to a less than 100% yield on the current reaction scale. XRD analysis was performed, confirming GaN formation. Appropriate peak shifting was observed in the XRD pattern, indicating inclusion of Er within the GaN matrix.

Example 7: Gallium Nitride Doped with 0.1 mol% Erbium

The method of Example 5 was used, but the quantity of erbium was changed to 0.1 mol% (0.061 g). High conversion rates were observed, but some product adhered to the reaction boat, contributing to a less than 100% yield on the current reaction scale. XRD analysis was performed, confirming GaN formation. Appropriate peak shifting was observed in the XRD pattern, indicating inclusion of Er within the GaN matrix.

Example 8: Green Light Emission from Erbium-doped GaN Powder

The direct observation of a strong green emission from erbium-doped GaN powder is reported in this Example. Gallium nitride was doped with erbium *in situ* during preparation of the erbium-doped GaN.

Methods and Materials:

The starting materials included 99.9999% pure gallium, 99.999% pure bismuth shot, 99.9% pure erbium ingots and 99.9999% pure ammonia gas. Purity of solid materials can be determined by GDMS (wt.% purity). An ammonia purifier was used to remove residual water vapor and oxygen from the ammonia gas.

Twenty-five grams of gallium was mixed with 1 mol% of erbium in a quartz tube. Bismuth (1 mol%) was added as a wetting agent. The quartz tube was then loaded into a vertical furnace. After purging the tube with argon (Ar) gas for one hour, the sample was heated under flowing Ar. When the melt temperature reached 1000 °C, the gas source was switched from Ar to ammonia (NH₃). The furnace was maintained at a constant temperature for 3-5 hours. The sample was then cooled to room temperature under flowing NH₃. No residual metal Ga or Er was observed by ocular inspection. No further etching was necessary to remove unreacted metals. The material was crushed and slightly ground with a mortar and pestle.

Removal of the bismuth wetting agent from the GaN:Er powder was achieved by heating the powder to 1030 °C under flowing NH₃ gas for three hours. At this temperature, the bismuth equilibrium vapor pressure is about 1200 Pa, more than 1000 times greater than that of Ga or Er. Bismuth was easily removed by evaporation while the NH₃ prevented GaN decomposition.

Results and Analysis:

Erbium-doped GaN (GaN:Er) powder was examined by x-ray diffraction (XRD) using Cu K α radiation. FIG. 10 shows the XRD pattern of GaN:Er powder after bismuth removal. The XRD pattern of the GaN:Er powder indicates a wurtzite structure. The peaks of this XRD pattern correspond well with those of a hexagonal GaN reported in the ASTM X-ray powder data file (PDF card 50-0792). No free gallium, erbium, or other phases were detected.

The (0002) peak of FIG. 10 is stronger than the (10 $\bar{1}$ 1) peak. FIG. 11 illustrates a scanning electron micrograph (SEM) picture of the GaN:Er powder. The SEM picture of the powder particle surface morphology provides an explanation for the stronger (0002) peak. The SEM image shows the particle size distributed from 1 μ m to 10 μ m, with a majority at around 5 μ m. While several particle morphologies can be observed (plates, polyhedra and needles), the predominant morphology is plate. The aspect ratios of the plates range from 10 to 50. The strong (0002) orientation indicated in XRD is likely caused by the alignment of the plates during the XRD sample preparation.

Considering that the ionic radius of Er³⁺ is 1.75 Å compared to 1.30 Å for Ga³⁺, the erbium concentration in GaN cannot be high under equilibrium conditions. However, erbium has very high solid solubility in Ga at high temperature. Shkol'nikova noted that the erbium solubility in gallium increased from 0.5% to 2.13% (mass fraction) with a temperature increase of 450 °C to 650 °C (T. M. Shkol'nikova, et al. *Zhurnal Fizicheskoi Khimii* **1972**, 46(3), 804). Erbium solubility in Ga can reach 8% at 800°C. In the GaN:Er powder synthesis process, erbium can fully dissolve into the gallium melt at high temperature under argon before flowing NH₃ is applied. The NH₃ reacts with molten gallium immediately when the gas is switched to NH₃. The yield of the powder synthesis was greater

than 99% within one hour. It is believed that the lateral growth rate of GaN in this process is very high. Under this high growth rate, erbium can easily be incorporated into the GaN structure instead of forming precipitates or microparticles. The bismuth wetting agent prevents GaN crust formation during the process.

Photoluminescence (PL) characterization was performed by exciting a sample of GaN:Er with an argon laser at a wavelength of 496.5 nm (2.5eV), corresponding to energy smaller than the GaN band gap (3.4eV). PL excitation resulted in green emission from the Er:GaN powder. Room temperature PL at visible wavelengths is shown in FIG. 12. Two major emissions were observed in the green region, with the strongest lines at 537.5 nm and 557.8 nm. Green emission at 537 nm is one of the characteristic emissions due to a $4f-4f$ inner shell transition of Er^{3+} ions and is attributed to a transition from $^2H_{11/2}$ to the ground state $^4I_{15/2}$. The 558nm emission corresponds to the transition from $^4S_{3/2}$ to $^4I_{15/2}$. The full width at half maximum (FWHM) of the main component of these transitions is close to 3 nm, which corresponds to an energy width of ~13 meV.

Electron probe microanalysis (microprobe) was used to analyze the erbium element distribution in the GaN particles. A GaN particle around 20 μm in width was selected for analysis. FIG. 13 shows the microprobe mapping measurement results. Erbium is distributed across the entire GaN particle, and the erbium concentration is fairly constant. The two areas of higher erbium concentrations are believed to result from erbium precipitates.

Discussion:

Green light emission has been directly obtained from erbium-doped GaN powder. Erbium was successfully incorporated into a GaN powder through the reaction of molten gallium and erbium with ammonia gas at 1000 °C, using bismuth as a wetting agent. Photoexcitation with an argon laser resulted in strong green emissions from two narrow lines at 537 and 558 nm, identified as erbium transitions from the $^2H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ ground state. X-ray diffraction indicated that the erbium-doped GaN powder has a wurtzite structure. Microprobe analysis revealed that erbium is distributed evenly in the powder particles.

This Example illustrates a process for doping Group III nitride powders with rare earth metals. The 4f luminescence of rare earth elements can be excited via minority-carrier injection in a 4f-doped pn junction or Schottky diode. Rare earth metal-doped Group III nitride powder can be dispersed into polymers and spin-coated on different substrates. Accordingly, materials are thus provided for the development of full color optical displays in a cost-efficient manner.

Example 9: Red Light Emission from Europium-doped GaN Powder

This Example describes a high yield process to produce gallium nitride (GaN) powder doped with europium. Europium (Eu) was incorporated *in situ* into GaN powder through the reaction between a molten alloy of Ga and Eu along with NH_3 at 1000 °C using Bi as a wetting agent. This procedure provides a method to produce a GaN:Eu phosphor with high yield and low cost. Strong red light emission was observed from this powder when it was optically excited either above- or below the GaN bandgap, or by an electron beam.

Room temperature photoluminescence (PL) measurements were conducted on GaN:Eu powders with different Eu concentrations. The maximum PL intensity was obtained at a Eu concentration of 1.25 mol%. Cathodoluminescence (CL) spectra at room temperature exhibited several detailed transitions in the 530 – 630 nm range.

Materials and Methods:

The starting materials used for making the GaN:Eu powder included 99.9999% pure gallium, 99.999% pure bismuth shot, 99.9% pure europium ingot, and 99.9999% pure ammonia. As a note of caution, Eu_2O_3 can be formed if Eu is exposed to air because Eu can react with oxygen at room temperature.

Twenty-five grams of Ga were mixed with 0.5-3 mol% of Eu and 3 mol% Bi in a glove box. The mixture was sealed into a quartz tube under vacuum, then heated to 830 °C for several hours to form an alloy. As the temperature is reduced, it is expected that Eu and Ga form the intermetallic compound EuGa_4 , while Bi reacts with Eu to form either EuBi or a GaBi alloy according to the published phase diagrams (*Desk handbook: Phase Diagram for Binary Alloys*, H. Okamoto, ed.

(ASM International, 2000)). After the tube cooled to room temperature, the product was transferred to the quartz tube reaction vessel. The quartz reaction tube was then loaded into a vertical furnace, evacuated and back filled with pure Ar gas, then heated under flowing Ar. When the melt temperature reached the appropriate reaction temperature of 1000 °C, the gas was switched from Ar to NH₃. At this temperature the entire charge was molten, in accordance with the published phase diagrams. At about five hours the alloy had completely converted into powder.

After the reaction was complete, the tube was allowed to cool to room temperature under flowing NH₃. The final product obtained from this process was a mass of powder without any visible metal remaining. No further etching steps are needed to remove unreacted metals. The powder mass can be removed easily from the quartz tube and ground into a finer powder. To remove the Bi, the powder was annealed at 1030 °C for one to four hours to evaporate the Bi under flowing NH₃, which prevents the powder from decomposing. At this temperature, the Bi equilibrium vapor pressure is about 10³ and 10⁶ times higher than that of pure Ga and Eu respectively, and much higher than the metal vapor pressures of their nitrides. Bi serves as a crucial wetting agent to help the conversion from Ga into GaN and to prevent the crust formation which is typically observed in GaN powder synthesis processes. The detailed synthetic procedures and mechanism has been discussed in other papers. For example, a high yield synthetic procedure to prepare high purity GaN powder using Bi as a wetting agent was recently developed (H. Wu, J. Hunting, K. Uheda, L. Lepak, P. Konkapaka, F. J. DiSalvo, and M. G. Spencer, *J. Crystal Growth* **2005**, 279, 303, incorporated by reference in its entirety). In addition, erbium has been incorporated into GaN powder (H. Wu, C. B. Poitras, M. Lipson, M. G. Spencer, J. Hunting, and F. J. DiSalvo, *Appl. Phys. Lett.* **2005**, 86, 191918, incorporated by reference in its entirety), and the emission of green light was reported when the powder was optically excited below the GaN bandgap.

Results and Analysis:

X-ray diffraction (XRD) analysis was performed on the GaN:Eu powder. No elemental Eu, Ga, Bi or EuN were detected in any of the samples with the various Eu concentrations. The peaks in the measured XRD pattern matched the

respective GaN peaks reported in the ASTM X-ray powder data file. A scanning electron microscopy (SEM) image exhibited particle sizes distributed from 1 μm to 5 μm , with a majority around 3 μm . Several particle morphologies were observed, including flakes, polyhedra and needles. The particles were highly faceted and hexagonal structure was clearly observed. Many layers in the particle could be observed indicating that the particles were grown layer by layer. The lateral growth rate was much higher than the *c*-direction growth rate. It was apparent that the GaN:Eu powder synthesized had very high crystalline quality.

Photoluminescence (PL) characterizations were performed with a HeCd laser (325 nm) and Ar laser (457.9 nm), which provide above and below bandgap excitations respectively. All PL measurements were performed at room temperature. Strong red light emitted from the powder when it was pumped with either the above- or below bandgap laser. The red color was mainly due to the 621 nm peak which was the strongest of the Eu emissions.

A series of PL spectra were conducted under HeCd laser excitation from GaN powders with different Eu concentration including a pure GaN powder sample without any Eu. The energy transfer from GaN host material to the Eu^{3+} ions was evident. The 366 nm peak corresponding to the GaN band edge emission decreased dramatically when Eu was introduced into the powder. The emission peaks of the Eu^{3+} ions intensified with increasing Eu concentration up to 1.25%, and weakened for higher doping concentrations. The decrease of the GaN band edge peak emission indicated increased energy transfer from the GaN to the Eu^{3+} ions. For the Eu emission, the decrease in emission for doping concentrations higher than 1.25% was potentially due to cross-relaxation between Eu^{3+} - Eu^{3+} ions. In these experiments, 1.25 mol% of Eu provided the greatest intensity with regard to red light emission. The FWHM for 621 nm peaks was about 2.2 nm and showed relative constancy for various Eu concentrations.

Cathodoluminescence (CL) was measured at room temperature. The excitation source was a 3 KeV electron beam focused on a 5mm diameter spot. FIG. 14 is a CL spectrum for GaN powder with 1% Eu. Both GaN band edge emission and Eu^{3+} ions emission at 621 nm were detected. The Eu ions emission at

621 nm, however, was much stronger and sharper compared to the GaN bandedge emission at 362 nm. The FWHMs were 1.6 and 14.2 nm for the 621 and 362 nm peaks, respectively. It was noted that there were several sharp peaks from 530 to 620 nm in the spectrum. Each of these peaks were reproduced in samples with different Eu concentrations. This indicates the high crystalline quality of the host particles. Some of these peaks can be attributed to the transitions reported in the literature and which have been marked in the FIG. 14. Other peaks in the spectrum are believed to be transitions from other 5D_j to the 7F_j levels. These peaks in the CL spectrum can provide much information for understanding the energy transfer processes between the Eu^{3+} ions and the GaN host.

Discussion:

The synthesis of, and the structural and optical emission characteristics of, Eu-doped GaN powder have been described. Europium was doped *in situ* into the GaN powder during the synthetic process. Strong red emission was observed from the powder when it was optically excited by both below- and above the bandgap of the host material, and by electron beam, at room temperature. Opportunities for low cost electroluminescent devices or hybrid structures are possible due to the powder form of this material.

Example 10: Gallium Nitride Doped with 1 mol% Cerium

In this example, Cerium was added to the reaction mixture to produce a Cerium-doped GaN powder. The method of Example 2 was used, except where noted below. The reactants were metal gallium (25 g), bismuth (2.271 g (3 mol %)), cerium (Ce) (1.507 g (1 mol%)), and purified ammonia gas. The reaction temperature was 1000 °C, the reaction time was 5 hours, and the NH_3 flow rate was 500 sccm. A quartz reaction vessel was used to contain initial reactants.

The Ga-Ce-Bi alloy was prepared as follows. Cerium was formed into small particles in a glove box under an Ar atmosphere. The metal reactants (Ga, Ce and Bi) were transferred into a small quartz tube and the tube was sealed to maintain an Ar atmosphere. The quartz tube and contents were placed in a furnace. The temperature was gradually increased to 780-830 °C as the furnace was purged with

Ar gas. The quartz tube was agitated through vibration to facilitate mixing and alloy formation. The metals were heated for 1-2 hours to ensure a uniform and homogeneous alloy was formed in the quartz tube. The alloy was transferred a reaction vessel in a glove box and was sealed. Care was taken at all times to prevent exposure of the Ce with nitrogen and oxygen gases.

Results: the Ga-Ce-Bi alloy was fully converted into a GaN powder doped with Ce within 5 hours. The color of the powder formed was light gray, and weighted 32.725 grams. XRD analysis was performed, confirming GaN formation.

Example 11: Gallium Nitride Doped with 1.5 mol% Cerium

The method of Example 9 was used, except that the quantity of cerium was changed to 1.5 mol% (2.261 g). High conversion rates were observed, but some product adhered to the reaction boat, contributing to a less than 100% yield for this reaction scale. XRD analysis was performed, confirming GaN formation. Appropriate peak shifting was observed in the XRD pattern, indicating inclusion of Ce within the GaN matrix.

Example 12: Gallium Nitride Doped with 0.5 mol% Cerium

The method of Example 9 was used, except that the quantity of cerium was changed to 0.5 mol% (0.754 g). High conversion rates were observed, but some product adhered to the reaction boat, contributing to a less than 100% yield on the current reaction scale. XRD analysis was performed, confirming GaN formation. Appropriate peak shifting was observed in the XRD pattern, indicating inclusion of Ce within the GaN matrix.

Example 13: Gallium Nitride Doped with 1 mol% Cerium

In this example, Cerium was added to the reaction mixture to produce a Cerium-doped GaN powder. The method of Example 2 was used, except where noted below. The reactants were metal gallium (25 g), bismuth (2.271 g (3 mol %)), cerium (Ce) (1.507 g (1 mol%)), and purified ammonia gas. The reaction temperature was 1000 °C, the reaction time was 5 hours, and the NH₃ flow rate was

500sccm. Metal Ga ingot, Ce powder and Bi shots were added into the reaction tube. A quartz reaction vessel was used to contain initial reactants.

Results: the Ga-Ce-Bi alloy was fully converted into a GaN powder doped with Ce within 5 hours. The color of the powder formed was light gray, and weighted 32.725 grams. XRD analysis was performed, confirming GaN formation.

Example 14: Gallium Nitride Doped with 1 mol% Cerium in a Boron Nitride Tube

In this example, Cerium was added to the reaction mixture to produce a Cerium-doped GaN powder. The method of Example 2 was used, except where noted below. The reactants were metal gallium (25 g), bismuth (2.271 g (3 mol %)), cerium (Ce) (1.507 g (1 mol%)), and purified ammonia gas. The reaction temperature was 1000 °C, the reaction time was 5 hours, and the NH₃ flow rate was 500 sccm. Metal Ga ingot, Ce powder and Bi shots were added into the reaction tube. A boron nitride (BN) reaction vessel was used to contain initial reactants.

Results: the Ga-Ce-Bi alloy was fully converted into a GaN powder doped with Ce within 5 hours. The color of the powder formed was light gray, and weighted 32.725 grams. XRD analysis was performed, confirming GaN formation.

All publications, patents, and patent documents herein are incorporated by reference, as though individually incorporated by reference. The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

What is claimed is:

1. A method for making Group III nitrides, the method comprising:
contacting a mixture comprising a Group III element and one or more wetting agents selected from the group consisting of bismuth, germanium, tin, and lead, in any combination,
with a nitrogen atom source to form a Group III nitride composition.
2. The method of claim 1 wherein the mixture is heated to a temperature sufficient to liquefy at least a portion of the mixture comprising the Group III element.
3. The method of claim 1 or 2 wherein the Group III element is gallium.
4. The method of claim 1 or 2 wherein the Group III element is boron.
5. The method of claim 1 or 2 wherein the Group III element is aluminum.
6. The method of claim 1 or 2 wherein the Group III element is indium.
7. The method of claim 1 or 2 wherein the Group III element is thallium.
8. The method of any one of claims 1-7 wherein the wetting agent is bismuth.
9. The method of any one of claims 1-7 wherein the wetting agent is germanium.
10. The method of any one of claims 1-7 wherein the wetting agent is tin.
11. The method of any one of claims 1-7 wherein the wetting agent is lead.
12. The method of any one of claims 1-7 wherein the wetting agent is antimony.

13. The method of any one of claims 1-7 wherein the wetting agent is tellurium.
14. The method of any one of claims 1-7 wherein the wetting agent is polonium.
15. The method of any one of claims 1-7 wherein the wetting agent is two or more of bismuth, germanium, tin, or lead, or a compound thereof, in any combination
16. The method of any one of claims 1-15 wherein the Group III element is in the form of shot or one or more ingots.
17. The method of any one of claims 1-16 wherein the wetting agent is in the form of shot or one or more ingots.
18. The method of any one of claims 1-17 wherein the Group III element is greater than about 99% pure by weight.
19. The method of any one of claims 1-17 wherein the Group III element is greater than about 99.9% pure by weight.
20. The method of any one of claims 1-17 wherein the Group III element is about 99.9999% pure by weight.
21. The method of any one of claims 1-20 wherein the wetting agent is greater than about 99% pure by weight.
22. The method of any one of claims 1-20 wherein the wetting agent is greater than about 99.9% pure by weight.

23. The method of any one of claims 1-20 wherein the wetting agent is greater than about 99.99% pure by weight.
24. The method of any one of claims 1-20 wherein the wetting agent is about 99.999% pure by weight.
25. The method of any one of claims 1-24 wherein the Group III element and the wetting agent are present in a molar ratio of about 1:1 to about 500:1.
26. The method of any one of claims 1-24 wherein the Group III element and the wetting agent are present in a molar ratio of about 2:1.
27. The method of any one of claims 1-24 wherein the Group III element and the wetting agent are present in a molar ratio of about 5:1.
28. The method of any one of claims 1-24 wherein the Group III element and the wetting agent are present in a molar ratio of about 20:1.
29. The method of any one of claims 1-24 wherein the Group III element and the wetting agent are present in a molar ratio of about 100:1.
30. The method of any one of claims 1-24 wherein the Group III element and the wetting agent are present in a molar ratio of about 200:1.
31. The method of any one of claims 1-30 wherein the mixture is heated to at least the monotectic temperature of the composition.
32. The method of any one of claims 1-30 wherein the mixture is heated to at least the consolute temperature of the composition.

33. The method of any one of claims 1-30 wherein the mixture is heated to at least about 262 °C.
34. The method of any one of claims 1-30 wherein the mixture is heated to at least about 650 °C.
35. The method of any one of claims 1-30 wherein the mixture is heated to at least about 900 °C.
36. The method of any one of claims 1-30 wherein the mixture is heated to about 1000 °C.
37. The method of any one of claims 1-30 wherein the mixture is heated up to about 1500 °C.
38. The method of any one of claims 1-30 wherein the mixture is heated to no greater than about 1100 °C.
39. The method of any one of claims 1-38 wherein the nitrogen atom source is a gas.
40. The method of any one of claims 1-38 wherein the nitrogen atom source is ammonia.
41. The method of any one of claims 1-38 wherein the nitrogen atom source is ammonia gas.
42. The method of any one of claims 1-41 wherein the nitrogen atom source has been treated to remove impurities.

43. The method of any one of claims 1-41 wherein the nitrogen atom source has been treated to remove water and oxygen.
44. The method of any one of claims 1-39 wherein the nitrogen atom source is not ammonia.
45. The method of any one of claims 1-38 wherein the nitrogen atom source is hydrazine.
46. The method of any one of claims 1-38 wherein the nitrogen atom source is an ammonium halide.
47. The method of any one of claims 1-38 wherein the nitrogen atom source is ammonium hydroxide.
48. The method of any one of claims 1-38 wherein the nitrogen atom source is an alkyl substituted amine or ammonium salt.
49. The method of any one of claims 1-38 wherein the nitrogen atom source is a nitrogen-containing organometallic compound.
50. The method of any one of claims 1-49 wherein the mixture is contacted with the nitrogen atom source by contacting the nitrogen atom source to the surface of the mixture.
51. The method of any one of claims 1-49 wherein the mixture is contacted with the nitrogen atom source by contacting the nitrogen atom source to the interior of the mixture.
52. The method of any one of claims 1-51 wherein the mixture is heated for at least 30 minutes.

53. The method of any one of claims 1-51 wherein the mixture is heated for about 1-20 hours.

54. The method of any one of claims 1-51 wherein the mixture is heated for about 3-6 hours.

55. The method of any one of claims 1-51 wherein the mixture is heated for about 5 hours.

56. The method of any one of claims 1-51 wherein the mixture is heated for up to ten days.

57. The method of any one of claims 1-56 wherein the Group III-nitride composition is produced in greater than about 50% purity by weight.

58. The method of any one of claims 1-56 wherein the Group III-nitride composition is produced in greater than about 75% purity by weight.

59. The method of any one of claims 1-56 wherein the Group III-nitride composition is produced in greater than about 95% purity by weight.

60. The method of any one of claims 1-56 wherein the Group III-nitride composition is produced in greater than about 99% purity by weight.

61. The method of any one of claims 1-56 wherein the Group III-nitride composition is produced in greater than about 99.5% purity by weight.

62. The method of any one of claims 1-61 wherein the Group III element and the wetting agent are contacted to form the mixture.

63. The method of any one of claims 1-62 wherein the mixture comprises a metal alloy comprising the Group III element and the wetting agent.
64. The method of any one of claims 1-63 further comprising cooling the mixture.
65. The method of any one of claims 1-63 further comprising cooling the mixture to ambient temperature.
66. The method of any one of claims 1-65 further comprising forming the Group III-nitride composition into a powder.
67. The method of any one of claims 1-65 further comprising forming the Group III-nitride composition into a powder by crushing.
68. The method of claim 66 wherein the powder is heated under a gas.
69. The method of claim 66 wherein the powder is heated under ammonia gas.
70. The method of any one of claims 68-69 wherein the powder is heated to at least about 800 °C.
71. The method of any one of claims 68-69 wherein the powder is heated to at least about 1000 °C.
72. The method of any one of claims 68-69 wherein the powder is heated to about 1030 °C.
73. The method of any one of claims 68-69 wherein the powder is heated up to about 1500 °C.

74. The method of any one of claims 68-73 wherein the powder is heated for at least 30 minutes.

75. The method of any one of claims 68-73 wherein the powder is heated for about 1-24 hours.

76. The method of any one of claims 68-73 wherein the powder is heated for about 5 hours.

77. The method of any one of claims 68-73 wherein the Group III-nitride composition is produced in greater than about 99.9% purity by weight.

78. The method of claim 66, further comprising contacting the powder with one or more solvents, and one or more oxidants that oxidize the wetting agent, to form a solution of an oxidized wetting agent, followed by separating the oxidized wetting agent from the powder.

79. The method of claim 78, further comprising removing any remaining oxidant by dissolution or evaporation.

80. The method claim 78 or 79 wherein one solvent is an alkyl, cycloalkyl, or aryl, optionally substituted with one or more polar groups, wherein the alkyl or cycloalkyl is optionally partially unsaturated, wherein the alkyl or cycloalkyl is optionally interrupted with one or more oxy, amino, or thio groups, and wherein the polar groups are one or more hydroxyl, amino, thio, or halo groups.

81. The method of any one of claims 78-80 wherein the one or more solvents comprise ethanol.

82. The method of any one of claims 78-81 further comprising heating the solution.

83. The method of claim 82 wherein the heating occurs at a reflux temperature of the composition.
84. The method of claim 82 or 83 wherein the heating occurs for from about one hour to about two days.
85. The method of claim 78 wherein the oxidant comprises a halogen.
86. The method of claim 78 wherein the oxidant is iodine.
87. The method of claim 78 wherein the separating occurs by filtration.
88. The method of any one of claims 1-87 wherein the Group III element and wetting agent are in a vessel that is purged with a gas.
89. The method of any one of claims 1-87 wherein the Group III element and wetting agent are in a vessel that is purged with an inert gas.
90. The method of any one of claims 1-87 wherein the Group III element and wetting agent are in a vessel that is purged with purified nitrogen gas.
91. The method of any one of claims 1-87 wherein the Group III element and wetting agent are in a vessel that is purged with purified argon.
92. The method of any one of claims 88-91 wherein the purging occurs for at least 10 minutes.
93. The method of any one of claims 88-91 wherein the purging occurs for about 1-4 hours.

94. The method of any one of claims 88-91 wherein the purging occurs for about 1.5 hours.
95. The method of claim 39 wherein the gas is passed over or through the mixture at a flow rate of about 100-900 sccm.
96. The method of claim 39 wherein the gas is passed over or through the mixture at a flow rate of about 200-800 sccm.
97. The method of claim 39 wherein the gas is passed over or through the mixture at a flow rate of about 400 sccm.
98. The method of claim 39 wherein the gas is passed over or through the mixture at a flow rate of about 500 sccm.
99. The method of claim 39 wherein the gas is passed over or through the mixture at a flow rate of about 600 sccm.
100. The method of any one of claims 68-87 wherein the Group III-nitride composition is produced in greater than about 99% purity by weight.
101. The method of any one of claims 68-87 wherein the Group III-nitride composition is produced in greater than about 99.5% purity by weight.
102. The method of any one of claims 68-87 wherein the Group III-nitride composition is produced in greater than about 99.9% purity by weight.
103. The method of claim 88 wherein the vessel is within a furnace or the vessel is a furnace.

104. The method of any one of claims 1-103 wherein the mixture is agitated by stirring, mixing, irradiating, shaking, or a combination thereof.
105. The method of any one of claims 68-87 wherein the powder is a crystalline Group III-nitride composition.
106. The method of claim 105 wherein the crystalline Group III-nitride composition is substantially hexagonal polycrystalline GaN.
107. The method of claim 105 wherein the crystalline Group III-nitride composition is substantially cubic polycrystalline GaN.
108. The method of any one of claims 68-87 wherein the powder is comprised of Group III-nitride composition crystalline plates of about 0.1 to about 50 μm in diameter.
109. The method of any one of claims 68-87 wherein the powder is comprised of Group III-nitride composition crystalline plates of about 1 to about 20 μm in diameter.
110. The method of any one of claims 1-109 wherein the Group III-nitride composition produced comprises single crystals.
111. The method of any one of claims 1-109 wherein the mixture further comprises a dopant.
112. The method of any one of claims 1-109 wherein the mixture further comprises one or more dopants selected from the group consisting of beryllium, magnesium, manganese, molybdenum, silicon, zinc, cerium, samarium, dysprosium, erbium, europium, promethium, thulium, ytterbium, and yttrium, or compounds thereof, in any combination.

113. The method of any one of claims 1-109 wherein the mixture further comprises one or more dopants selected from the group consisting of boron, aluminum, and indium, or a compound thereof, in any combination.
114. The method of claim 103 wherein the vessel is a quartz vessel.
115. The method of claim 103 wherein the vessel is made of or is lined with boron nitride, graphite, SiC coated graphite, TaC coated graphite, molybdenum, tungsten, or TaC.
116. The method of any one of claims 1-115 wherein the nitrogen atom source is not a gas.
117. The method of any one of claims 1-116 wherein the pressure has been reduced to as low as about 10 Torr.
118. The method of any one of claims 1-116 wherein the pressure has been increased to as high as about 10,000 Torr.
119. The method of claim 111 wherein the mixture emits green light when subjected to photoexcitation.
120. The method of claim 111 wherein the mixture emits yellow light when subjected to photoexcitation.
121. The method of claim 111 wherein the mixture emits red light when subjected to photoexcitation.

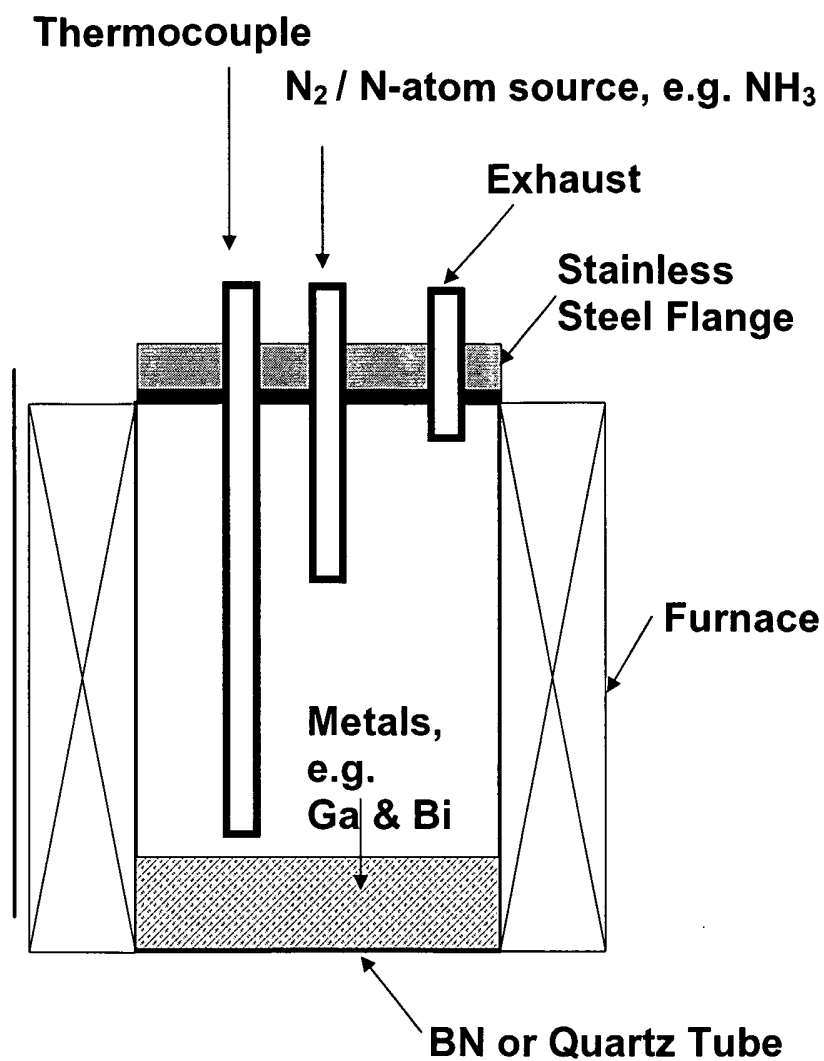


FIG. 1

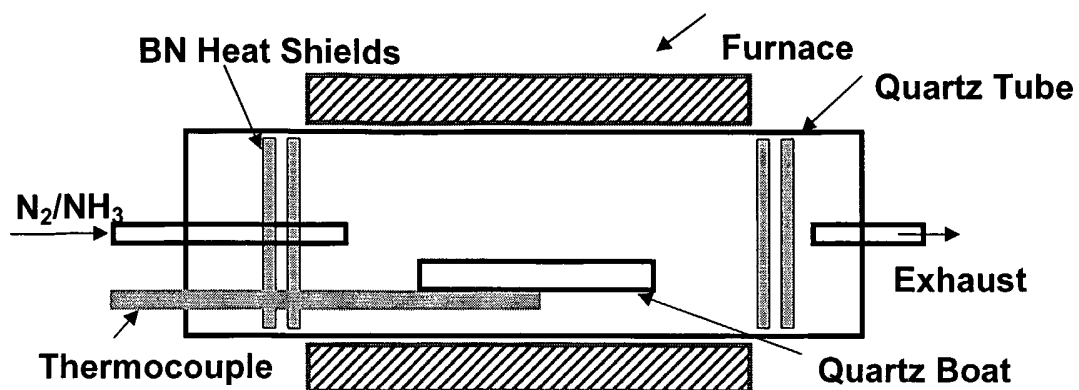


FIG. 2

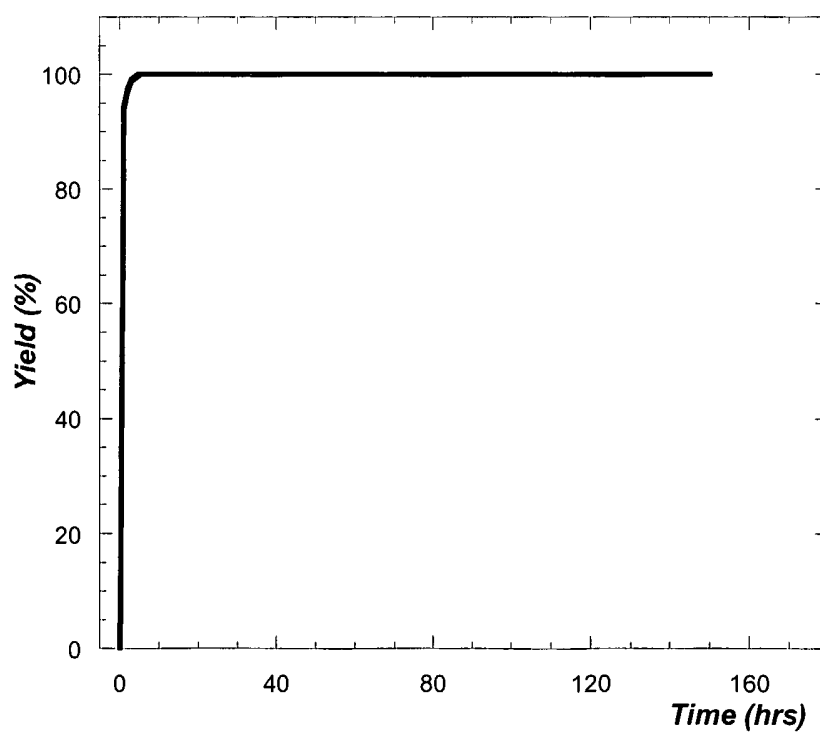


FIG. 3

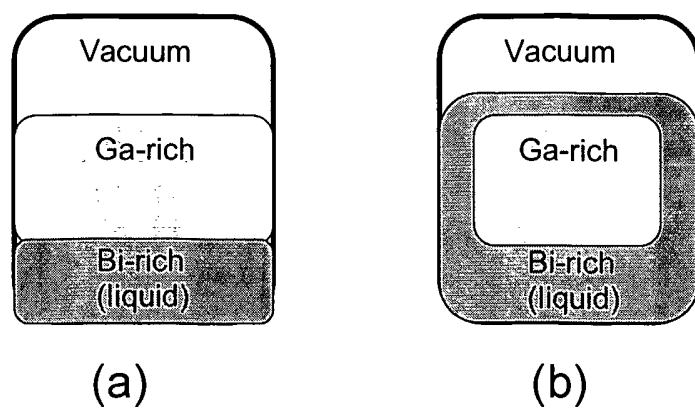


FIG. 4

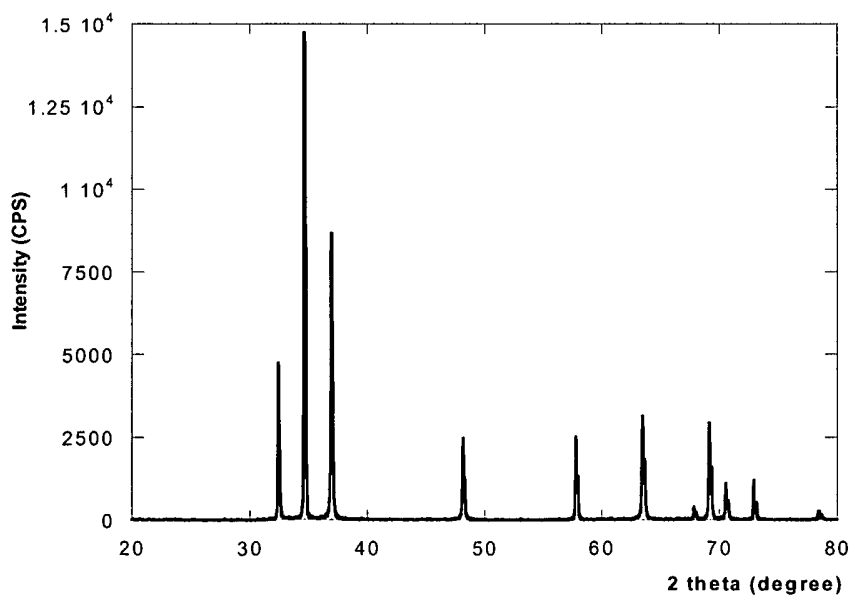


FIG. 5

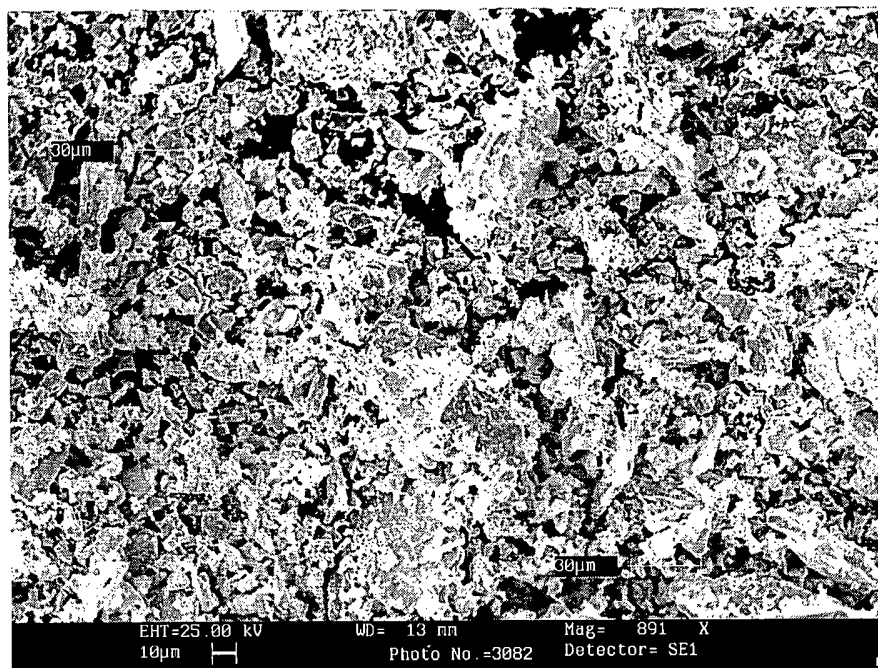


FIG. 6(a)

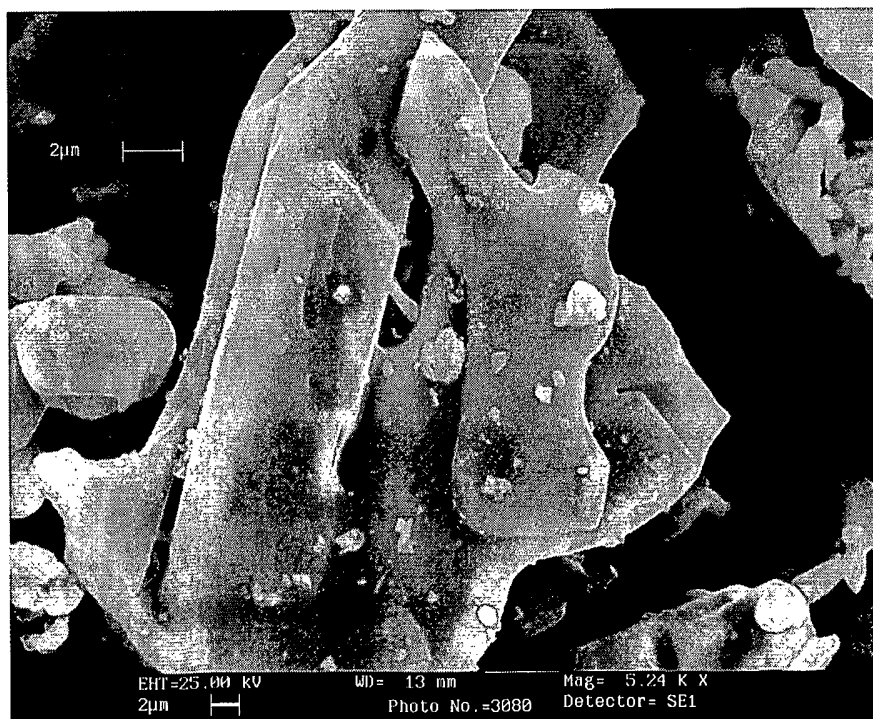


FIG. 6(b)

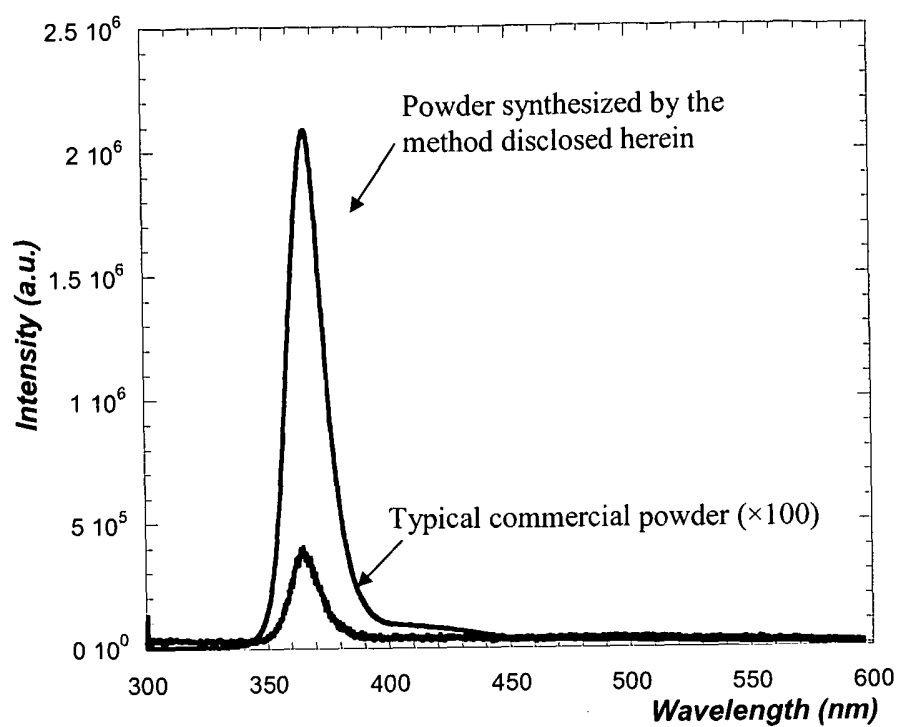


FIG. 7

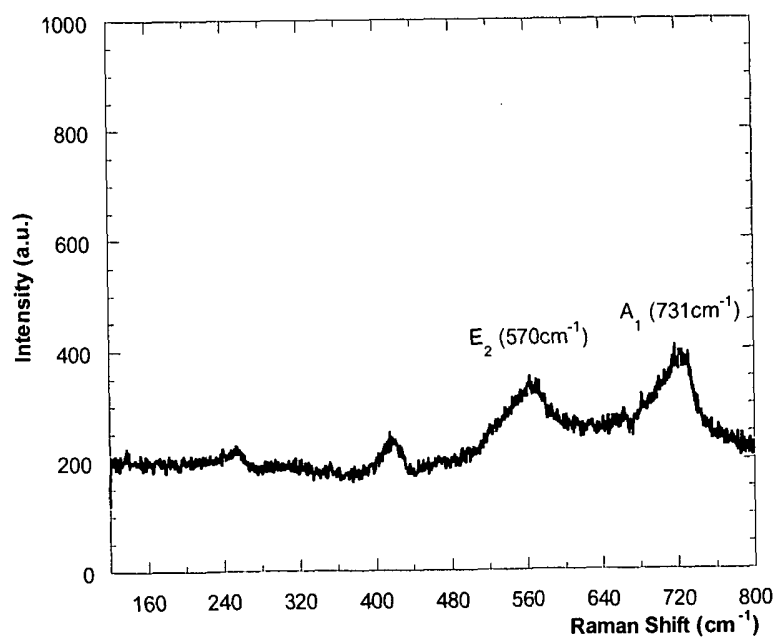


FIG. 8 (a)

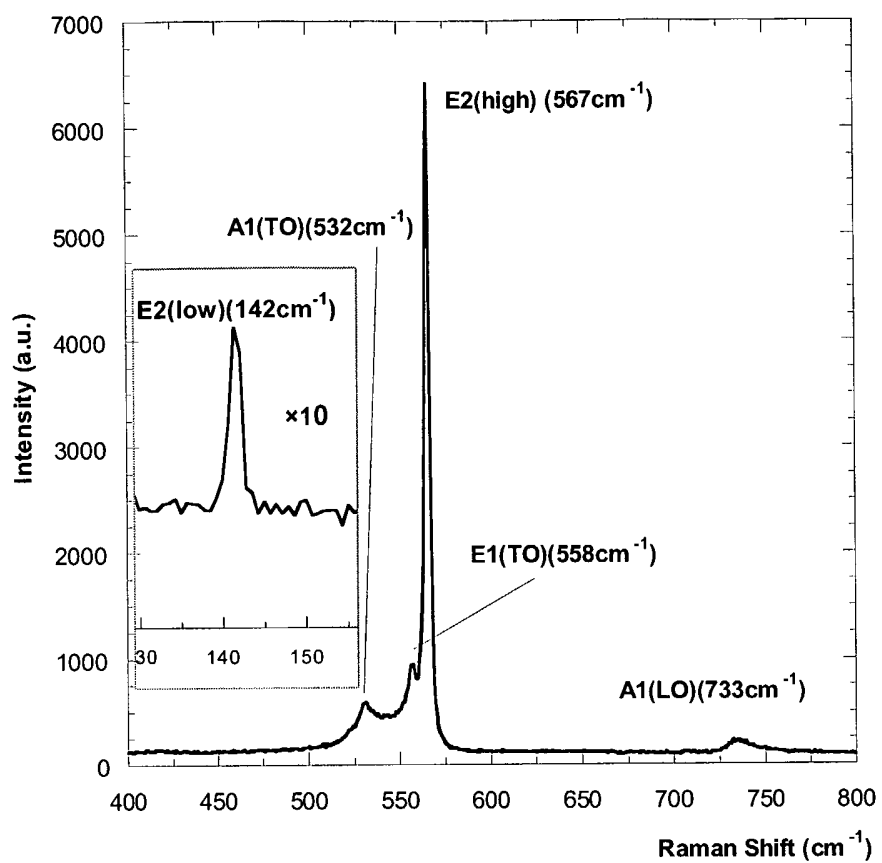
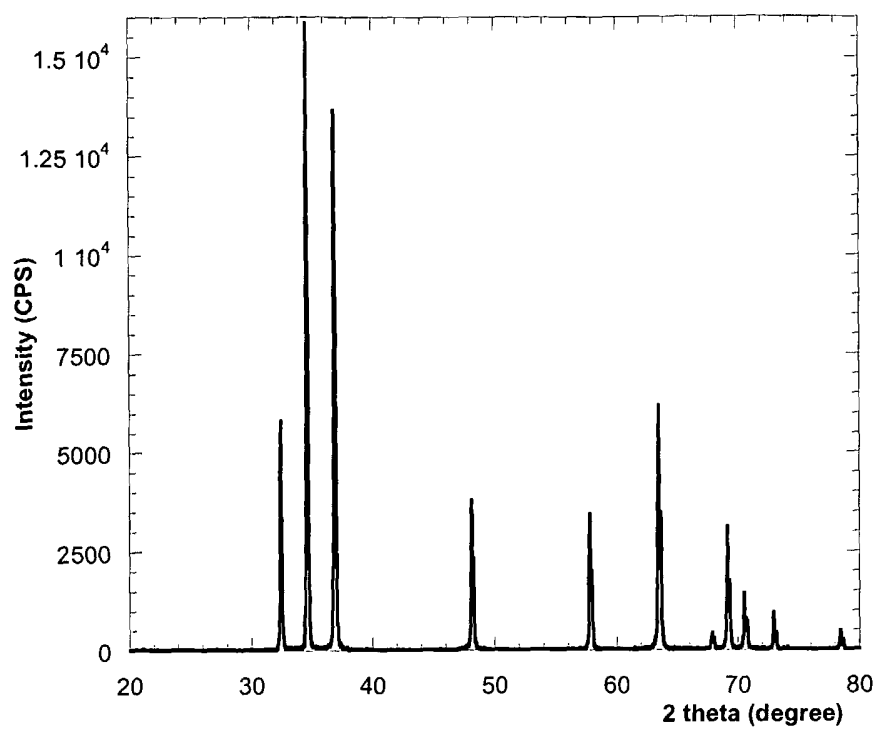


FIG. 8 (b)

**FIG. 9**

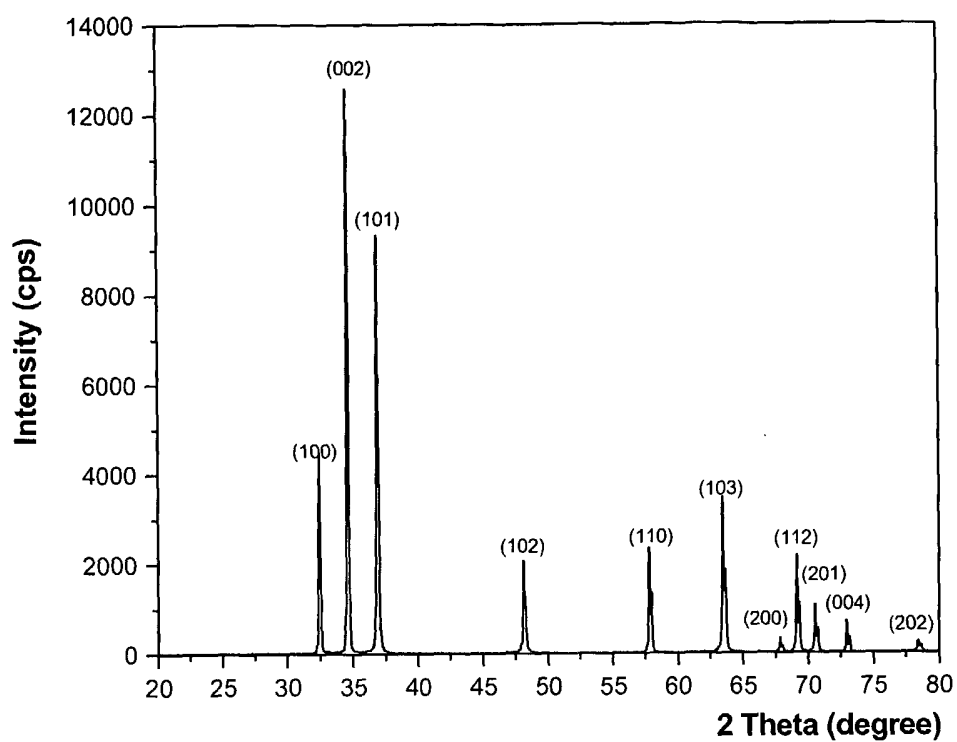


FIG. 10

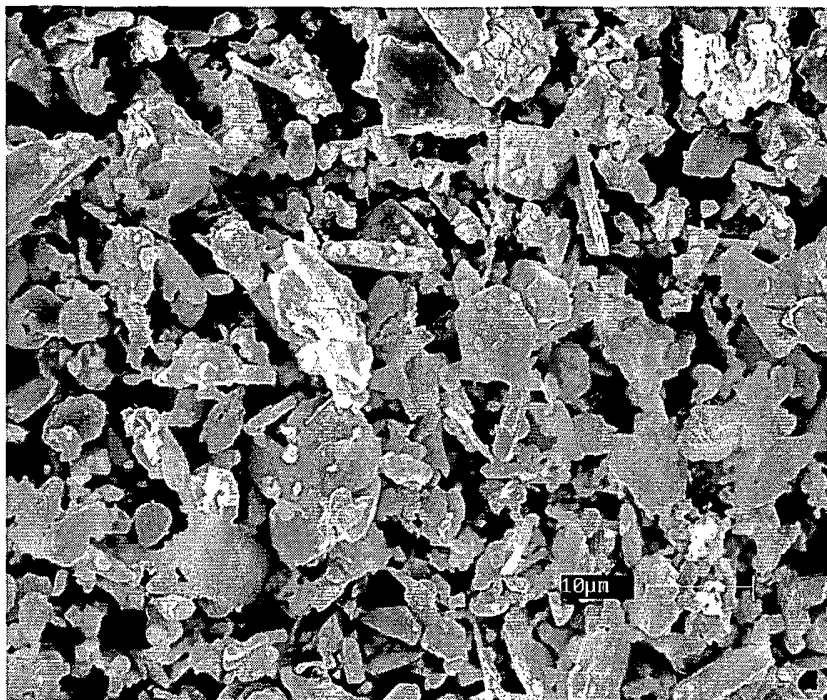


FIG. 11

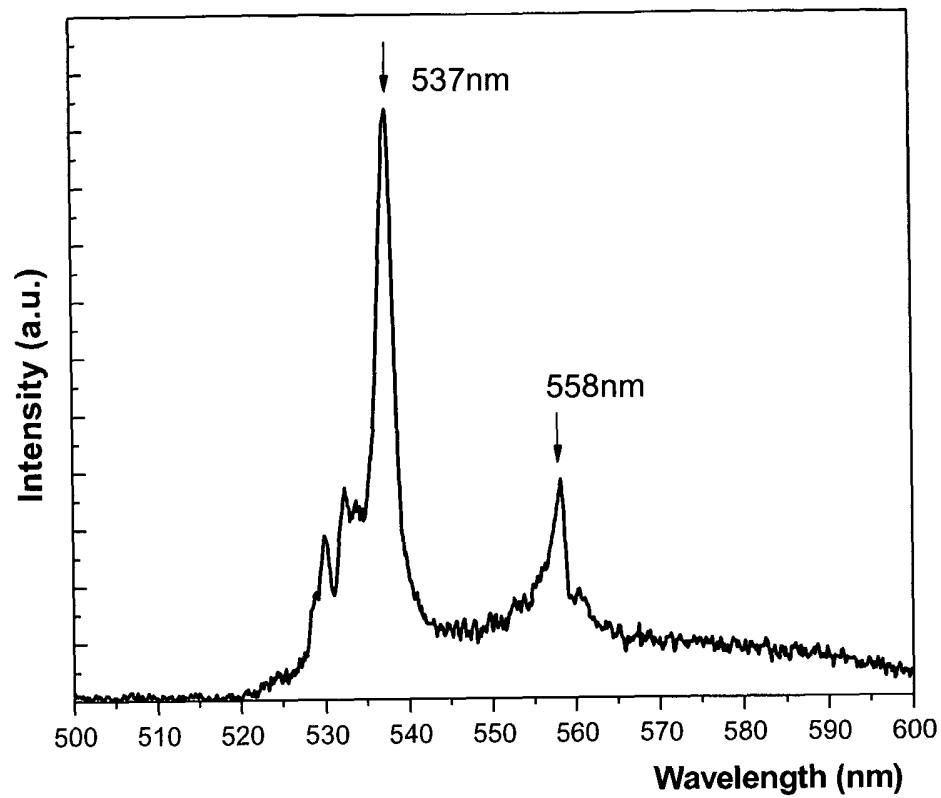


FIG. 12

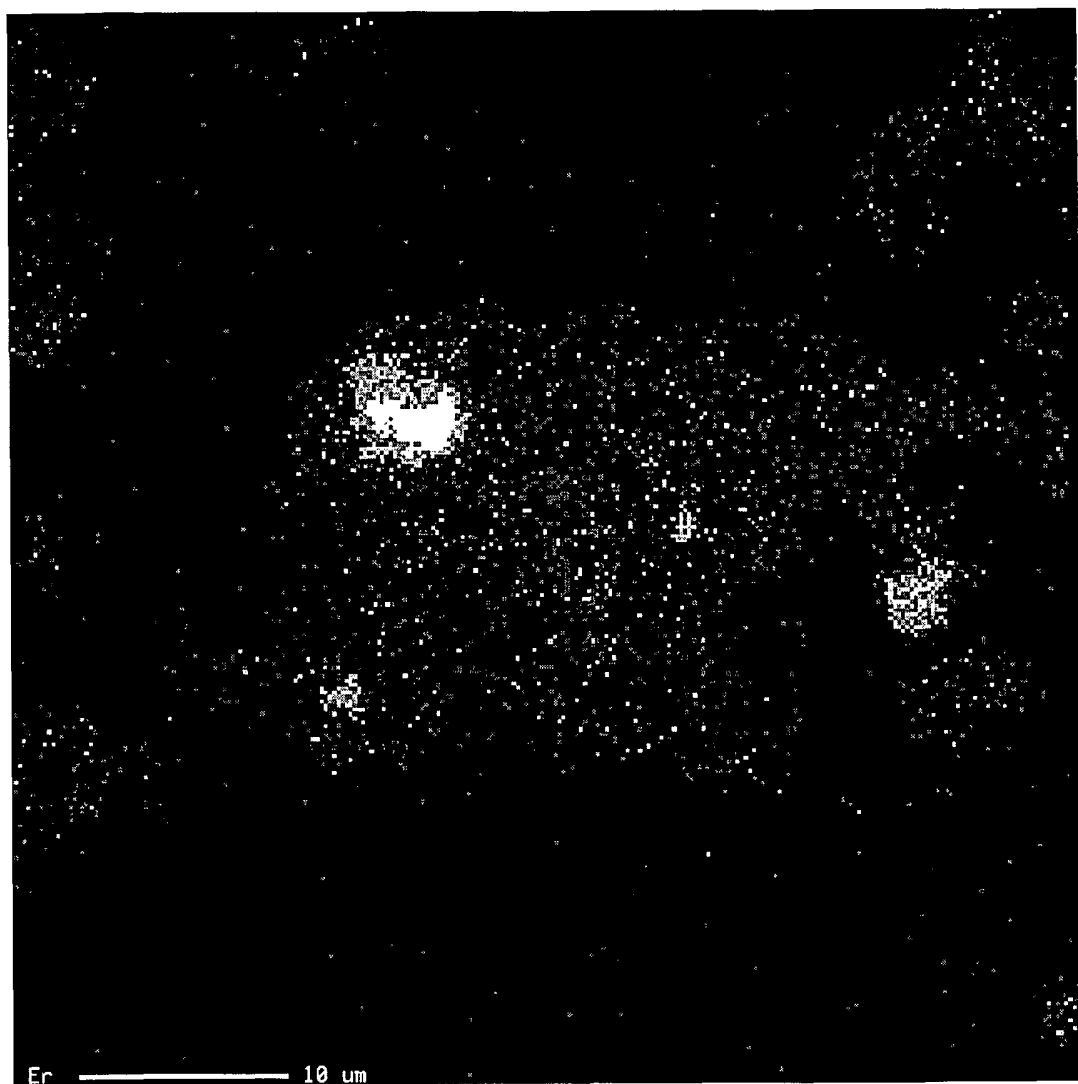


FIG. 13

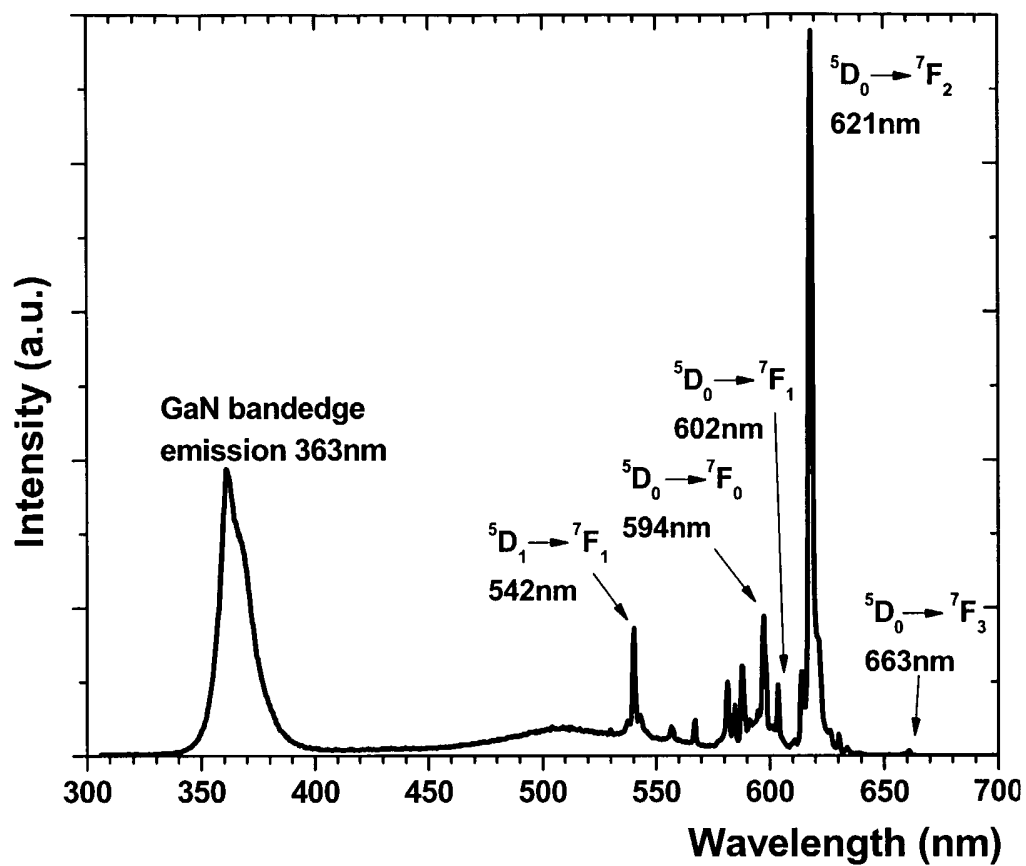


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/24427

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 35/00;C01B 21/064; C01B 25/00; C01B 9/00
US CL : 423/290,409,412

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)
U.S. : 423/290,409,412

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,406,677 B1 (CARTER et al) 18 June 2002 (18-06-2002).	1-15



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 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

26 September 2005 (26.09.2005)

Date of mailing of the international search report

07 DEC 2005

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Wayne Langel

Telephone No. 703-872-9206



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/24427

Box No. 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.: 16-121
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. 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:

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 additional fees, this Authority did not invite payment of any additional fees.
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 and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.