

Synthesis Routes and Characterization of High-Purity, Single-Phase Gallium Nitride Powders

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Synthesis of high-purity, single-phase gallium nitride powder has been achieved in a hot-wall tube furnace via (i) the reaction of gallium with ammonia (NH₃) and (ii) the conversion of gallium oxide (Ga₂O₃). For complete reaction, the optimum temperatures, NH₃ flow rates, and boat positions relative to the NH₃ inlet were 975°C, 400 standard cubic centimeters per minute (sccm), and 50 cm, respectively, for the gallium-NH₃ reaction, and 1050°C, 500 sccm, and 50 cm, respectively, for the Ga₂O₃ conversion. Polyhedra of various shapes were obtained from both processes; some rod-shaped crystals also were observed in the material derived from Ga₂O₃.

I. Introduction

THE recent fabrication of *p-n* junctions,¹ heterostructures,² quantum wells and lasers in thin-film structures containing gallium nitride (GaN),^{3,4} and the subsequent commercial realization of blue and green light-emitting diodes based on these structures have generated considerable interest and a growing number of research programs devoted to Group III-V nitrides. In the wurtzite form, GaN has a band gap of 3.45 eV (near the ultraviolet, UV, region) at room temperature. GaN also forms a continuous range of solid solutions with aluminum nitride (6.28 eV) and indium nitride (1.95 eV). Thus, optoelectronic devices having specifically engineered band gaps with energies from the visible to the deep UV region theoretically are possible with these materials. The wide band gaps of these materials and their strong atomic bonding also make them candidates for high-power, high-frequency, and high-temperature devices. Presently, GaN films are grown almost universally on foreign substrates, e.g., sapphire and SiC. The mismatches in lattice parameters result in significant densities ($\geq 10^8$ cm/cm⁻³) of dislocations in the films.⁵ As such, the availability of GaN bulk single crystals and wafers for homoepitaxial film growth has gained considerable importance. Crystal growth process routes applicable to GaN, e.g., sublimation and high-pressure solution methods, demand the availability of a high-purity, single-phase, well-characterized powder source.

The demand for GaN powder always has been very small, and research and development regarding production routes for this material have been very limited. The amount, purity, and cost of the commercially available GaN powder currently are limited, poor, and extreme, respectively. The available X-ray diffractometry (XRD) and crystallographic data for GaN* also are limited and date to 1938.⁶ These early data have a figure of merit of 14, which corresponds to an unassigned quality rating. As such, the objectives of the research reported below have

been the development of viable, thermodynamically based process routes for the synthesis of very-high-purity GaN powder and the characterization of the resulting materials.

II. Selection of Synthesis Routes

The first reported synthesis of GaN powder was achieved by Johnson *et al.*⁷ by flowing ammonia (NH₃) over molten gallium heated at temperatures of 900°–1000°C. Subsequent research by Pichugin and Yaskov⁸ substantiated the efficiency of this process route. Lorenz and Binkowski⁹ produced GaN powder by reacting gallium oxide (Ga₂O₃) with NH₃ in the temperature range of 600°–1100°C. Addamiano¹⁰ obtained GaN powder by heating fine particles of gallium phosphide (GaP) and gallium arsenide (GaAs) in a stream of hot NH₃ at temperatures of 1000°–1100°C. Conversion of crushed single-crystal GaAs to GaN was investigated by Isherwood and Wickenden;¹¹ in this route, an intermediate Ga₂O₃ phase was formed, which subsequently was nitrided in NH₃ to GaN in the temperature range of 700°–1000°C. No information was given in any of these studies regarding the purity of the prepared material.

In selecting methods for economically producing semiconductor-purity GaN powder, the instability of GaN to sublimation and the very low reactivity between gallium and nitrogen gas ($\Delta G_f = 31$ kJ/mol and $K_p = 0.004$ at 900°C, and $\Delta G_f = -18$ kJ/mol and $K_p = 17$ at 500°C; ΔG_f is the free energy of formation and K_p is the equilibrium constant) must be considered. Therefore, precursor selection and establishment of experimental parameters became an important issue. As the first step, the oxidation state of the sublimed or evaporated specie from candidate condensed phases was determined from the free-energy differences of the solid and the evaporated or sublimed specie. In this manner, the correct state and composition of the starting materials were determined. Subsequently, the thermodynamic data for these species were used in the free-energy calculations for the process routes that were considered to produce GaN powder. The results of this procedure are summarized in Table I.

The free energy of reaction (ΔG_r) values at the approximate temperatures that would be used in GaN powder production (600°–1000°C) for reactions (1)–(6) (see Table I) are mostly positive and, thus, indicate that they would not occur. Therefore, with the exception of reaction (5), these reactions were ruled out. As mentioned above, Addamiano¹⁰ was able to obtain GaN powder from GaP and GaAs by firing these compounds in flowing dry NH₃. However, these compounds were not considered for precursor materials in the present program because of their higher price per gram relative to commercially available GaN powder. Furthermore, the conversion of GaAs requires an intermediate conversion to Ga₂O₃, because a thin layer of GaN, formed on the surface of GaAs, prevents complete conversion of GaAs to GaN.¹² This additional step increases the possibility of contamination. However, the same problem was not reported for GaP; the evaporation of phosphorus has been a major problem in this conversion process.⁶

Reactions (7)–(9) are the most suitable reactions for the synthesis of pure GaN, when the thermodynamic, kinetic, and economic criteria are considered. Among these candidate routes,

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*Powder Diffraction File, Card No. 2-1078. International Centre for Diffraction Data, Newtowne Square, PA, 1938.

Table I. Free Energy of Reaction Values for Possible Reactions to Produce GaN

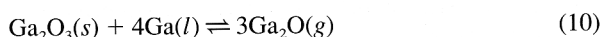
Reaction	Number	Temperature, <i>T</i> (°C)	Free energy of reaction, ΔG_r (kJ/mol)
$\text{GaBr(g)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{GaN(s)} + \text{HBr(g)} + \text{H}_2\text{(g)}$	(1)	300–1000	–17–+25
$\text{GaI(g)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{GaN(s)} + \text{HI(g)} + \text{H}_2\text{(g)}$	(2)	300–1000	–8–+33
$\text{GaCl}_3\text{(g)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{GaN(s)} + 3\text{HCl(g)}$	(3)	300–1000	+54–+4
$\text{GaF}_3\text{(s)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{GaN(s)} + 3\text{HF(g)}$	(4)	300–1000	+138––25
$\text{Ga}_2\text{O}_3\text{(s)} + 2\text{NH}_3\text{(g)} \rightleftharpoons 2\text{GaN(s)} + 3\text{H}_2\text{O(g)}$	(5)	300–1000	+205–+200
$\text{GaCl(g)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{GaN(s)} + \text{HCl(g)} + \text{H}_2\text{(g)}$	(6)	300–1000	–30–+17
$\text{Ga(l)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{GaN(s)} + \frac{3}{2}\text{H}_2\text{(g)}$	(7)	300–1000	–54––50
$\text{Ga}_2\text{O(s)} + 2\text{NH}_3\text{(g)} \rightleftharpoons 2\text{GaN(s)} + \text{H}_2\text{O(g)} + 2\text{H}_2\text{(g)}$	(8)	300–1000	–33–0
$\text{Ga}_2\text{O(g)} + 2\text{NH}_3\text{(g)} \rightleftharpoons 2\text{GaN(s)} + \text{H}_2\text{O(g)} + 2\text{H}_2\text{(g)}$	(9)	300–1000	–196––96

reaction (7) offers a viable method whereby the resulting GaN powder can be as pure as the starting reactants. The availability of ultrapure gallium metal, coupled with the recent advances in the reduction of water and oxygen in the NH_3 to <1 ppm, allow the achievement of very-high-purity, single-phase GaN powder at reasonable cost.

Reaction (7) was used in this research with several modifications to the experimental procedures used by the earlier investigators. An important product of these studies was a marked refinement of the existing crystallographic and XRD data as well as related microstructural information for the GaN powders discussed below.

Reaction (5) also was investigated experimentally as an alternative synthesis route. This route has been used by researchers to describe the conversion of Ga_2O_3 (i.e., $\beta\text{-Ga}_2\text{O}_3$) to GaN. However, thermodynamic calculations from available data show that this reaction will not occur at temperatures where GaN production is feasible. The reaction is favorable only if reaction (8) is embedded in this process.

The reactant phase of $\text{Ga}_2\text{O(g)}$ in reaction (9) is not commercially available but may be formed from a mixture of Ga(l) and $\text{Ga}_2\text{O}_3\text{(s)}$ via the reaction



A 4:1 molar mixture of gallium and Ga_2O_3 reportedly¹³ has a Ga_2O vapor pressure of 0.2 torr (~ 27 Pa) at 800°C and 10 torr (~ 1333 Pa) at 1000°C. However, this production scheme was not considered because of the difficulty of capturing the ultrafine GaN powder that forms in the gas phase. Furthermore, this two-step process involving reaction (10) increases the possibility of contamination of the GaN powder by oxygen and other elements.

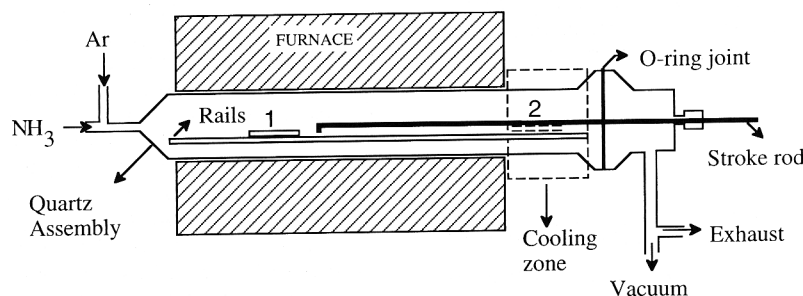
III. Experimental Procedure

To produce GaN powder via reaction (7) in Table I, precursor materials of 99.99% pure molten gallium metal, contained in pure-quartz reaction boats, and 99.9999% pure NH_3 gas were reacted in a horizontal tube furnace 4 cm in diameter and 90 cm long, with a quartz liner. A schematic of the system is shown in Fig. 1. A three-dimensional matrix of boat position (intervals of 5 cm from the NH_3 inlet), NH_3 flow rate (200–500 standard

cubic centimeters per minute, sccm), and boat temperature (800°–1200°C) was used to determine the optimum conditions for complete conversion of gallium to GaN. The gallium was heated to the desired temperature prior to reaction under flowing NH_3 . To minimize GaN decomposition, on completion of each experiment, the samples were pulled into the cooling zone of the furnace with the stroke rod and rapidly cooled (10°C/min) to room temperature (see Fig. 1) under an increased flow of NH_3 (typically 1000 sccm). No free gallium or other phase was observed in the XRD patterns of the GaN powder synthesized in the temperature range of 900°–1050°C. The rapid formation of a gas-permeable GaN layer was achieved within this temperature range, such that the unreacted metal was exposed continuously to NH_3 . Similar studies in the temperature range of 1050°–1200°C resulted in a small, but X-ray detectable, amount of free gallium in the powder, presumably as a result of the decomposition of the GaN. At temperatures <900°C, a GaN crust formed on the surface of the liquid gallium, regardless of the flow rate of NH_3 (400–1000 sccm) or the reaction time (1–4 h), and stopped the reaction. For our system, the optimum conditions of boat position, boat temperature, and NH_3 flow rate for the complete conversion of the gallium to GaN were 50 cm from the NH_3 inlet, 400 sccm, and 975°C, respectively. The material produced under these conditions was selected for characterization via XRD and scanning electron microscopy (SEM).

After removal from the boats, the material was crushed and slightly ground in an agate mortar. The XRD patterns of the GaN powder were obtained using a powder diffractometer (Model D/MAX-IIA, Rigaku Co., Tokyo, Japan) equipped with an incident-beam monochromator to obtain $\text{CuK}\alpha$ radiation. The conditions of 0.02° 2θ per step, with a counting time of 4 s, were used for the diffraction scans. Systematic machine errors were determined using a 99.999% pure internal silicon standard. Error corrections were made subsequently on the actual d -spacings obtained from the XRD data. Appleman and Evans¹⁴ and TREOR¹⁵ cell-refinement methods were used to perform least-squares refinements of the data. Further details of the XRD analysis procedures are given in Ref. 16.

The conversion of Ga_2O_3 also was conducted in the system shown in Fig. 1. The precursor materials of 99.9999% pure NH_3 and 99.999% pure Ga_2O_3 powder were used. The Ga_2O_3 was loaded into quartz boats and heated in the temperature range of

**Fig. 1.** Schematic of GaN powder production system.

800°–1100°C for 1–2 h under an NH_3 flow rate of 500 sccm. Complete conversion of Ga_2O_3 to GaN was observed at 1050°C. X-ray scans were conducted on powder obtained from different locations in the boat to confirm complete conversion. Experiments in the temperature range of 800°–1000°C yielded material that showed low-intensity, broad GaN X-ray peaks.

SEM images of the crushed GaN powders produced by both methods were obtained using a field emission microscope (Model 6400, JEOL, Tokyo, Japan) at 5 kV. The data obtained from these studies regarding the average particle size and morphology are very important for the next step in the crystal growth research, which is the consolidation of the powder into solid shapes having densities near theoretical. All powders also were analyzed by inductively coupled plasma (ICP) and secondary ion mass spectroscopy (SIMS) techniques to determine the presence and concentrations of impurities.

IV. Results and Discussion

The GaN produced via reaction of molten gallium with flowing NH_3 at 975°C was porous and off-white. No visible interaction between the boat and the gallium metal or GaN was discerned. Because gallium can be purchased in very high purities, semiconductor-quality GaN is now possible. An analysis of 30 common elements via the ICP technique revealed only 100 ppm manganese and 50 ppm magnesium as detectable impurities. The only disadvantage of the procedure used is that it is a batch process, which limits the quantity of material produced in a given run to the size of the furnace and the container for the metal.

An SEM image typical of the optimized GaN powder produced from gallium is shown in Fig. 2(A). The particle-size distribution is narrow (1–5 μm), with a majority of the particles being $\sim 1 \mu\text{m}$. The morphology of the particles is a mixture of various polyhedra and rounded particles. The XRD results show a marked improvement in the crystallographic quality relative to existing data. The unit-cell data and the data from a representative XRD pattern of single-phase GaN powder are presented in Tables II and III, respectively. The powder diffraction file reports a figure of merit of $F_{19} = 14$, with 19 planes indexed; the diffraction data determined in this research and presented in Table III have a figure of merit of $F_{23} = 175$, where all observed planes were indexed in the range of 30°–130°. These results have been accepted by the International Centre for Diffraction Data for consideration as the new powder diffraction standard for GaN.

In the second synthesis route, complete conversion of the Ga_2O_3 to GaN was achieved in flowing NH_3 . No other phases were observed in the X-ray spectra. As before, no visible interaction between the quartz boat and the Ga_2O_3 or the

Table II. Unit-Cell Data for GaN

Data property	Value
Lattice parameter	
<i>a</i>	3.1891(8) Å
<i>c</i>	5.1855(2) Å
Crystal system	Hexagonal
Coordination number, <i>Z</i>	2
Space group	$P6_3mc$ (186)
Cell volume, <i>V</i>	45.672(2) Å ³
Density, <i>D_x</i>	6.0886 g·cm ⁻³
Formula weight	83.7297 g
Figure of merit ¹⁵	$M_{23} = 374; F_{23} = 174$ (0.004579, 29)

GaN powder was detected. Analysis by ICP revealed no detectable impurities in the GaN. The SEM studies showed mainly submicrometer-sized particles with various polyhedral shapes, as well as a small percentage of rod-shaped forms 5–10 μm long (Fig. 2(B)). A close examination of these images revealed that the sizes and morphologies of the GaN particles were determined primarily by the Ga_2O_3 precursor.

As noted earlier, reaction (5) has a positive ΔG_r value for all temperatures used in this research. Thermodynamic calculations of several intermediate reactions have been made to explain the inconsistency between the experimental results and the positive ΔG_r value of reaction (5). The NH , NH_2 , NH_3 , H_2 , and N_2 species can be assumed to be present in our system at 1000°C because of the combustion of NH_3 gas. Thermodynamic data show that Ga_2O_3 , in the presence of H_2 , NH , or NH_2 , will be reduced to Ga_2O . Calculations of free energies for the reactions between NH , NH_2 , or NH_3 and Ga_2O are negative and, thus, result in the synthesis of GaN. Determination of the exact specie(s) that is (are) responsible for the conversion of Ga_2O_3 to GaN is not possible. The lifetimes of NH and NH_2 are extremely short in comparison to those of H_2 and NH_3 ; thus, the latter gases very likely control the reduction and nitridation reactions, respectively.

The GaN particles produced via oxide conversion may have unreacted cores containing significant concentrations of oxygen. However, a comparison of the SIMS data taken from GaN obtained by both routes did not show any significant difference in oxygen concentrations. A conservative estimate was made from the single-crystal sputtering rate of GaN to ensure that cores of the GaN particles were analyzed.

V. Summary

An economically viable process route has been established to produce high-purity, single-phase GaN powder via reaction

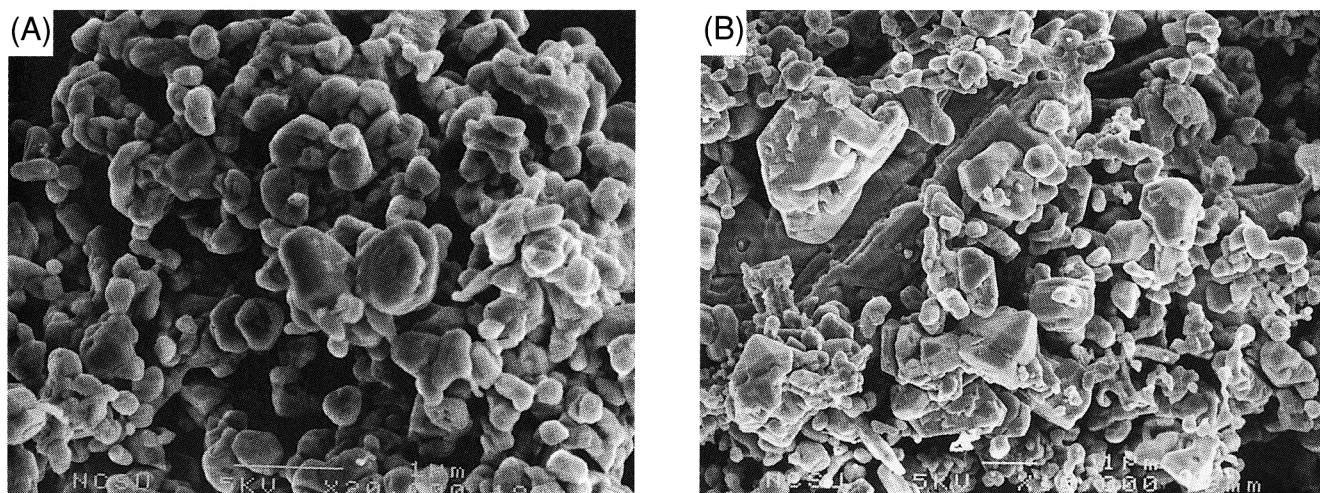


Fig. 2. SEM micrographs of GaN obtained (A) from gallium and NH_3 reaction and (B) conversion of Ga_2O_3 .

Table III. XRD Data for GaN

Experimental 2θ (degrees)	Relative intensity, I/I_0	Lattice spacing, d_{exp} (Å)	Miller indices, hkl	$\Delta 2\theta^*$ (degrees)
32.3904	56	2.762	100	-0.002
34.5702	45	2.593	002	-0.002
36.8465	100	2.437	101	0.000
48.0902	19	1.891	102	-0.001
57.7758	31	1.5945	110	+0.002
63.4492	27	1.4649	103	+0.019
67.8117	4	1.3809	200	+0.001
69.1040	22	1.3582	112	+0.005
70.5114	12	1.3345	201	-0.004
72.9062	3	1.2964	004	+0.003
78.3940	3	1.2186	202	+0.000
82.0349	2	1.1737	104	-0.009
91.1101	7	1.0790	203	-0.005
95.1200	3	1.0438	210	+0.010
97.6528	8	1.0234	211	-0.002
99.9511	5	1.0059	114	+0.004
105.0019	6	0.9709	105	+0.008
105.4025	5	0.9683	212	+0.001
109.1648	1	0.9452	204	-0.003
113.5807	4	0.9207	300	-0.011
119.0945	8	0.8936	213	+0.003
125.2224	4	0.8676	302	+0.000
126.0445	2	0.8644	006	-0.009

*Observed - calculated.

of liquid gallium metal with flowing NH_3 . An alternative method of producing GaN from Ga_2O_3 also was achieved. For the first route, the optimum temperature, NH_3 flow rate, and boat position in the hot-wall tube furnace relative to the NH_3 inlet for complete reaction were 975°C, 400 sccm, and 50 cm respectively. The analogous experimental parameters for the second route were 1050°C, 500 sccm, and 50 cm, respectively. Results from the SEM, SIMS, and ICP analysis techniques revealed that, although material purity and quality are suitable for our needs, the latter approach will necessitate conditioning the precursor oxide, because the particle morphology of the resulting GaN is not suitable for consolidation processes. XRD data obtained from the powder produced via the first route revealed that the GaN was single phase, with the following crystal data: $a = 3.1891$ Å, $c = 5.1855$ Å, space group = $P6_3mc$, $Z = 2$, and $D_x = 6.0886$ g·cm $^{-3}$.

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