Ammonothermal Conversion of Cyclotrigallazane to GaN: Synthesis of Nanocrystalline and Cubic GaN from [H₂GaNH₂]₃

Jolin A. Jegier,[†] Stuart McKernan,[†] Andrew P. Purdy,*[,‡] and Wayne L. Gladfelter*[,†]

Department of Chemistry and Center for Interfacial Engineering, University of Minnesota, Minneapolis, Minnesota 55455, and Naval Research Laboratory, Chemistry Division, Code 6120, Washington D.C. 20375-5342

Under ammonothermal conditions, cyclotrigallazane, [H₂GaNH₂]₃, was converted to nanocrystalline GaN. The coherent length of the GaN product could be controlled by manipulating reaction time and temperature. Nanocrystalline GaN powders with average crystallite sizes of 3−17 nm were produced in the temperature range of 150−450 °C. Analysis of the powders by XRD and TEM indicated that the nanocrystals possessed a structure composed of a random arrangement of cubic and hexagonal close packed planes. The addition of NH₄I to the reaction mixture resulted in the isolation of bulk samples of phase pure, cubic GaN at temperatures as low as 200 °C. The synthesis of the cubic phase was found to be temperature dependent, with mixtures of cubic and hexagonal GaN being produced at temperatures greater than 350 °C.

Introduction

Gallium nitride is a wide band gap semiconductor (3.45 eV) which has gained increased importance due to its use in blue light emitting devices. The synthesis of nanocrystalline GaN, and nanoscale materials in general, has also attracted increased attention due to the theoretical prediction[1−3] and experimental observation[4] that the band gap of these materials increases with decreasing particle size due to quantum confinement effects. Our laboratory reported the first synthesis of nanocrystalline GaN, via the solid-state pyrolysis of cyclotrigallazane, [H₂GaNH₂]₃.[5,6] Since this initial report, other researchers have developed alternative approaches to the synthesis of GaN nanocrystals including: the solid-state pyrolysis of [Ga(NH)₃/₂]∞,[7−9] the thermolysis of [Ga(NH)₃/₂]∞ in trioctylamine,[10] the solvothermal reaction of GaCl₃ and Li₃N,[11] the heterogeneous solution reaction between GaBr₃ and Li₃N,[12] a carbon nanotube confined reaction between Ga₂O and NH₃,[13] the detonation of Lewis base adducts of Ga-(N₃)₃,[4,14,15] and the thermal decompositions of [H₂GaN₃]ₙ and [H(Cl)GaN₃]ₙ.[16] Nanocrystalline GaN-PMMA[17] and GaN-silica aerogel[18] composites have also been synthesized.

One of the major difficulties encountered in the synthesis of nanocrystalline GaN involves synthetic control over the particle size of the product. While Fischer and co-workers have recently reported a measure of control over GaN crystallite size,[14,15] current synthetic methods typically do not lead to a satisfactory level of control over particle size or dispersity. This has led us to search for a more controlled, solution-based route for the synthesis of nanocrystalline GaN. Specifically, we were interested in the use of ammonothermal techniques, which have led to the synthesis of a wide variety of metal amides, imides, and nitrides as well as metastable phases of many materials unattainable through other methods.[19] We wish to report the use of ammonothermal techniques for controlling the coherent length of GaN powders derived from [H₂GaNH₂]₃. We also report the use of these techniques to synthesize GaN possessing the zinc blende structure. While the cubic phase of GaN had previously been observed in thin

† University of Minnesota.
‡ Naval Research Laboratory, Chemistry Division.
(1) Brus, L. E. *J. Chem. Phys* **1983,** *79,* 5566.
(2) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991,** *95,* 525.
(3) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 41.
(4) Frank, A. C.; Stowasser, F.; Miskys, C. R.; Ambacher, O.; Giersig, M.; Fischer, R. A. *Phys. Status Solidi A* **1998,** *165,* 239.
(5) Hwang, J.-W.; Hanson, S. A.; Britton, D.; Evans, J. F.; Jensen, K. F.; Gladfelter, W. L. *Chem. Mater.* **1990,** *2,* 342.
(6) Hwang, J.-W.; Campbell, J. P.; Kozubowski, J.; Hanson, S. A.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* **1995,** *7,* 517.
(7) Wells, R. L.; Janik, J. F. *Chem. Mater.* **1996,** *8,* 2708.
(8) Coffer, J. L.; Johnson, M. A.; Zhang, L.; Wells, R. L.; Janik, J. F. *Chem. Mater.* **1997,** *9,* 2671.
(9) Coffer, J. L.; Zerda, T. W.; Appel, R.; Wells, R. L.; Janik, J. F. *Chem. Mater.* **1999,** *11,* 20.
(10) Micic, O. I.; Ahrenkiel, S. P.; Bertram, D.; Nozik, A. J. *Appl. Phys. Lett.* **1999,** *75,* 478.
(11) Xie, Y.; Qian, Y.; Wang, W.; Zhang, S.; Zhang, Y. *Science* **1996,** *272,* 1926.
(12) Wells, R. L.; Janik, J. F. *Eur. J. Solid State Inorg. Chem.* **1996,** *33,* 1079.
(13) Han, W.; Fan, S.; Li, Q.; Hu, Y. *Science* **1997,** *277,* 1287.
(14) Frank, A. C.; Stowasser, F.; Sussek, H.; Pritzkow, H.; Miskys, C. R.; Ambacher, O.; Giersig, M.; Fischer, R. A. *J. Am. Chem. Soc.* **1998,** *120,* 3512.
(15) Frank, A. C.; Fischer, R. A. *Adv. Mater.* **1998,** *10,* 961.
(16) McMurran, J.; Kouvetakis, J.; Nesting, D. C.; Smith, D. J.; Hubbard, J. L. *J. Am. Chem. Soc.* **1998,** *120,* 5233.
(17) Gonsalves, K. E.; Carlson, G.; Rangarajan, S. P.; Benaissa, M.; Jose-Yacaman, M. *J. Mater. Chem.* **1996,** *6,* 1451.
(18) Goodwin, T. J.; Leppert, V. J.; Smith, C. A.; Risbud, S. H.; Niemeyer, M.; Power, P. P.; Lee, H. W. H.; Hrubesh, L. W. *Appl. Phys. Lett.* **1996,** *69,* 3230.
(19) Jacobs, H.; Schmidt, D. *Curr. Top. Mater. Sci.* **1982,** *8,* 381.

1004   *Chem. Mater., Vol. 12, No. 4, 2000*

Jegier et al.

films,[20-23] bulk samples have only recently been synthesized.[24]

Experimental Section

General Considerations. All synthetic manipulations were carried out with the strict exclusion of moisture and oxygen using standard Schlenk and glovebox techniques. Cyclotrigallazane, $[H_2GaNH_2]_3$,[25] was prepared as previously described. Ammonia (Air Products) was dried over Na^0 prior to use. Ammonium iodide was sublimed prior to use.

Ammonothermal Reactions. Ammonothermal reactions carried out at temperatures between 150 and 200 °C were conducted in a stainless steel Parr autoclave (model 1432HC) equipped with polyethylene/polypropylene O-rings and fitted with a Pyrex sleeve. The autoclave was heated in an aluminum block and the temperature was maintained using an Omega temperature controller, and the pressure was monitored using an Omega pressure transducer. Reactions at temperatures greater than 200 °C were conducted in 17.8 cm (5 mm o.d./3 mm i.d.) quartz tubes. After being charged, the tubes were flame-sealed and placed in a Leco MRA-114R pressure vessel. (Caution: glass tubes filled with liquid ammonia can burst unexpectedly at room temperature. Be sure to wear adequate eye, face, and hand protection.) The vessel was then pressurized to 10000 psi with distilled water using a Leco HR-1B hydrothermal system and heated in a furnace in a vertical orientation. All temperatures were measured in a thermowell near the bottom of the pressure vessel which typically stabilized 50 °C lower than the furnace temperature. The temperature gradient along the length of the reaction tube was approximately −10 °C/cm.[24]

X-ray. X-ray diffraction studies were conducted on a Siemens D5005 diffractometer using monochromatic (graphite) Cu Kα radiation. The average coherent length of the GaN powders was estimated using the Scherrer equation and the Jade software package (Materials Data Incorporated). Rietveld refinement of the cubic GaN diffraction pattern was accomplished using the RIQAS software package (Materials Data Incorporated).

Electron Microscopy. Specimens for TEM and SEM analysis were prepared by pulverizing the GaN powders in an agate mortar. Samples for SEM analysis were sprinkled on carbon tape. Samples for TEM analysis were sprinkled on lacey carbon coated copper grids. SEM images were obtained on a Hitachi S900 microscope. TEM studies were conducted on a Phillips CM30 microscope operating at 300 kV.

Synthesis of Nanocrystalline GaN. *Method A.* The autoclave was charged with $[H_2GaNH_2]_3$ (400 mg) and ammonia (~25 mL) was condensed into the autoclave at −78 °C. The autoclave was sealed and heated to 150 °C for 24 h reaching a pressure of 1740 psig. The autoclave was then cooled to 25 °C over a period of several hours and the NH_3 was slowly vented. The GaN product (244 mg) was isolated as an off-white powder and was found to have an average coherent length of 4 nm. Conducting the experiment at 150 °C (5 h) and 200 °C (5 h) produced off-white GaN powders, having coherent lengths of 3 and 4 nm, respectively.

Method B. A quartz tube was charged with $[H_2GaNH_2]_3$ (26 mg) and NH_3 was condensed into the tube at −196 °C. The tube was flame-sealed at a height of 14 cm (60% fill) and heated to 250 °C for 1000 min. The apparatus was cooled to ~200 °C over 2 h and removed from the furnace. After cooling

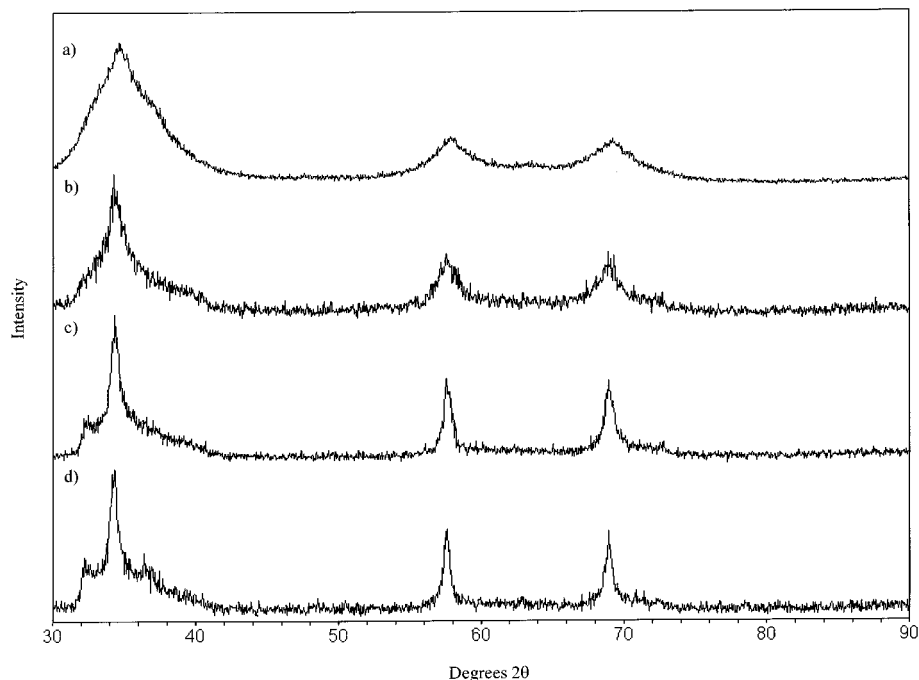(20) Neumayer, D. A.; Ekerdt, J. G. *Chem. Mater.* **1996**, *8*, 9.
(21) Paisley, M. J.; Sitar, Z.; Posthill, J. B.; Davis, R. F. *J. Vac. Sci. Technol. A* **1989**, *7*, 701.
(22) Sitar, Z.; Paisley, J.; Ruan, J.; Choyke, J. W.; Davis, R. F. *J. Mater. Sci. Lett.* **1992**, *11*, 261.
(23) Mizuta, M.; Fuieda, S.; Matsumoto, Y.; Kawamura, T. *Jpn. J. Appl. Phys.* **1986**, *25*, L945.
(24) Purdy, A. P. *Chem. Mater.* **1999**, *11*, 1648.
(25) Campbell, J. P.; Hwang, J.-W.; Young, V. G., Jr.; Von Dreele, R. B.; Cramer, C. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1998**, *120*, 521.

Table 1. Comparison of Nanocrystalline GaN Prepared under Various Conditions

precursor	conditions	T (°C)	t (min)	coherent length (nm)	phase
$[H_2GaNH_2]_3$	solid	600	240	6	nanocrystalline[a]
$[HGaNH]_n$		600	240	5	nanocrystalline[a]
$[H_2GaNH_2]_3$	ammonothermal	150	300	3	nanocrystalline[a]
GaN	annealed	600	240	3	nanocrystalline[a]
$[H_2GaNH_2]_3$	ammonothermal	200	300	4	nanocrystalline[a]
		150	1440	4	nanocrystalline[a]
		250	1000	8	nanocrystalline[a]
		350	1000	14	nanocrystalline[a]
		450	1000	17	nanocrystalline[a]
$[H_2GaNH_2]_3$	NH_3/NH_4I	200	1315	>1000	cubic
		260	940	>1000	cubic
		350	1000	>1000	cubic + hexagonal
		450	1000	>1000	cubic + hexagonal[b]
				>1000	cubic[c]

[a] Structure contains random arrangement of cubic and hexagonal close packed planes [b] Bottom of tube [c] Deposited on the wall at the middle of the tube

to 25 °C, the tube was removed from the pressure vessel, the liquid was decanted away from the product, and the tube was cooled to −196 °C. The tube was opened, and the pale yellow GaN powder was washed with ethanol and dried. The product was found to have a coherent length of 8 nm. Similar experiments were carried out at 350 and 450 °C, resulting in pale yellow GaN powders having coherent lengths of 14 and 17 nm, respectively.

Synthesis of Cubic GaN. The procedure was as for Method B above using $[H_2GaNH_2]_3$ (38 mg), NH_4I (38 mg), and NH_3 (59% fill). The tube was heated to 200 °C, resulting in the isolation of a pale yellow GaN product, which was found to possess the zinc blende structure. XRD [°2θ (I/I_o, *hkl*)] 34.26 (100, 111), 39.80 (27.5, 200), 57.66 (35.6, 220), 68.90 (28.7, 311), 72.45 (6.1, 222), 86.15 (4.2, 400). Similar reactions were carried out at 260, 350, and 450 °C. The reactions at 350 and 450 °C produced pale yellow mixtures of cubic and hexagonal GaN. At 450 °C, some of the material was deposited on the quartz near the middle of the tube and isolated as an orange powder. X-ray diffraction established this as pure cubic GaN. The powder remaining at the bottom of the tube was a mixture of cubic and hexagonal GaN.

Results

Conversion to Nanocrystalline GaN. Cyclotrigallazane, $[H_2GaNH_2]_3$, was converted to nanocrystalline GaN under ammonothermal conditions. Experiments were carried out at the temperatures and reaction times summarized in Table 1. Heating an ammonia solution of $[H_2GaNH_2]_3$ at 150 °C for 5 h in a steel autoclave resulted in the isolation of an off-white GaN powder. The product was found to have an average coherent length of 3 nm as estimated by line broadening in the X-ray diffraction pattern. Annealing the powder at 600 °C for 4 h under a N_2 atmosphere did not lead to growth of the nanocrystals as determined by XRD. An increase in coherent length of the product was observed by extending the reaction time (from 5 to 24 h) or by raising the reaction temperature (from 150 to 200 °C). Both experiments produced off-white GaN powders with average coherent lengths of 4 nm. The effect of reaction temperature on the coherent length of the GaN powders was further studied by conducting the reactions in sealed quartz tubes at temperatures ranging from 250 to 450 °C. The pale yellow GaN powders obtained from these experiments exhibited coherent lengths ranging from 8 nm (250 °C) to 17 nm (450 °C).

Figure 1. X-ray diffraction patterns of the nanocrystalline GaN produced from $[H_2GaNH_2]_3$ under ammonothermal conditions emphasizing the effect of reaction temperature on product coherent length. The diffraction patterns are of the nanocrystals produced at (a) 150 °C (4 nm), (b) 250 °C (8 nm), (c) 350 °C (14 nm), and (d) 450 °C (17 nm). Peak assignment (°2θ): 32.70 (100, h-GaN), 35.20 (002, h-GaN; 111, c-GaN), 36.53 (101, h-GaN), (57.68 (110, h-GaN; 220, c-GaN), 69.00 (112, h-GaN; 311, c-GaN).

X-ray diffraction patterns of the GaN powders are presented in Figure 1. The 3-nm GaN powder produced at 150 °C (Figure 1a) exhibited very broad diffraction peaks, and little information about the phase of the material could be elucidated. The 8-nm powder obtained at 250 °C (Figure 1b) exhibited diffraction peaks that were assigned to the 111, 200, 220, and 311 reflections calculated for GaN possessing the zinc blende structure.[5] The 14- and 17-nm GaN powders obtained at 350 and 450 °C, respectively (Figures 1c and 1d), also displayed diffraction peaks consistent with the zinc blende structure. Diffraction peaks were also present at 32.70 and 36.53 °2θ and were assigned to the 100 and 101 reflections of GaN having the wurtzite structure.[26] This suggested that there was a measurable amount of hexagonal material present in the sample.

TEM analysis was performed on the GaN sample produced at 450 °C (Figure 2). The sample was found to be polydisperse, comprised mainly of crystallites with an average size of 13 nm and a smaller number of particles as large as 150 nm. All of the particles examined exhibited a striped pattern. These striations were attributed to the presence of numerous stacking faults within the individual crystallites. The electron diffraction pattern of one of the nanocrystals (Figure 2, inset) supported this hypothesis. Shown is the 123 pattern of GaN having the zinc blende structure. The streaking of the diffraction spots parallel to the [111] direction was also indicative of a structure containing many defects such as stacking faults. Analysis of several clusters of nanocrystals over the entire TEM grid revealed particles with similar defect structures and electron diffraction patterns. This indicated that the sample was homogeneous and contained only disordered

nanocrystals (as opposed to discrete cubic and hexagonal phases).

Synthesis of Cubic GaN. The use of basic mineralizing agents such as MNH_2 (M = Li, K) had previously been shown to aid in reagent transport and product crystallization during the ammonothermal syntheses of various group 13 nitrides.[27−32] Acidic mineralizing agents such as NH_4I have also been shown to aid in the crystallization of various solid-state materials[27,33] including GaN,[24] and AlN.[32] The ammonothermal conversion of $[H_2GaNH_2]_3$ to GaN was conducted in the presence of NH_4I to assess its impact on this conversion. Thermolysis of a 1:1 mass ratio of $[H_2GaNH_2]_3$ and NH_4I in NH_3 at 200 °C resulted in the isolation of a pale yellow GaN powder possessing the zinc blende structure. Similar experiments were conducted at temperatures ranging from 260 to 450 °C, and the results are presented in Table 1. The experiment at 450 °C resulted in transport of ~50% of the product to the walls of the reaction tube, which was isolated as an orange powder. The color of the product obtained from these ammonothermal syntheses was sensitive to reaction conditions; it was previously noted that the use of different Ga sources and temperature programs led to the isolation of GaN powders which were gray, off white, yellow, orange, or green in color.[24] Due to the thermal gradient

(26) Powder Diffraction File, I.C.f.D.D., Swarthmore, PA, card no. 2-1078.

(27) Kolis, J. W.; Wilcenski, S.; Laudise, R. A. *Mater. Res. Soc. Symp. Proc.* **1998**, *495*, 367.
(28) Dwilinski, R.; Wysmolek, A.; Baranowski, J.; Kaminska, M. *Acta Phys. Pol., A.* **1995**, *88*, 833.
(29) Dwilinski, R.; Baranowski, J. M.; Kaminska, M. *Acta Phys. Pol., A* **1996**, *90*, 763.
(30) Dwilinski, R.; Doradzinski, R.; Garczynski, J.; Sierputowski, L.; Baranowski, J. M.; Kaminska, M. *Diamond Relat. Mater.* **1998**, *7*, 1348.
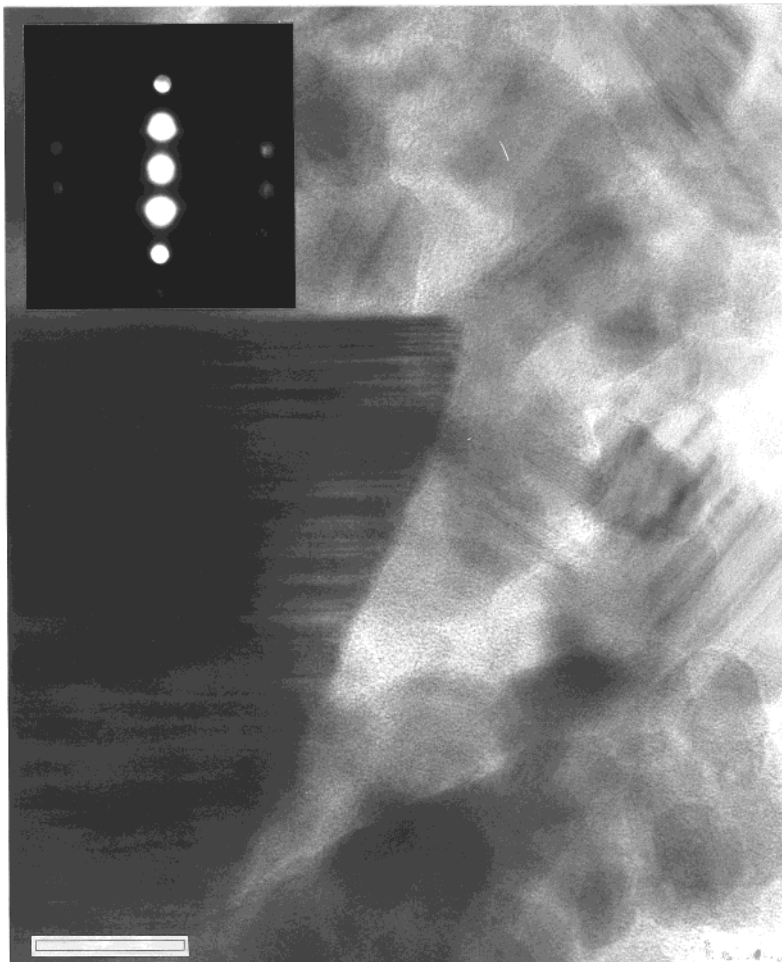(31) Peters, D. *J. Cryst. Growth* **1990**, *104*, 411.
(32) Peters, D. *Ceramic Powder Processing Science, Proc. 2nd Intern. Conf.* **1989**, 181.
(33) Purdy, A. P. *Chem. Mater.* **1998**, *10*, 692.

Figure 2. Transmission electron micrograph and corresponding electron diffraction pattern (123 orientation, inset) of the nanocrystalline GaN produced from $[H_2GaNH_2]_3$ at 450 °C. This sample was polydisperse and included 13-nm crystallites and a smaller number of crystallites up to 150 nm. The striped pattern appearance of the particles is due to the presence of numerous stacking faults within the individual crystallites. The scale bar represents 20 nm.

observed in the apparatus (see Experimental Section), the temperature of the reaction tube at the level where the material was deposited was ~360 °C.

The diffraction patterns of the samples synthesized at 200 and 260 °C (Figure 3a,b) showed that the samples consisted of relatively pure cubic GaN. The average coherent length was found to be >1 μm as estimated by the Scherrer equation. In addition to the peaks which could be indexed to GaN possessing the zinc blende structure, the diffraction patterns of the samples produced at 350 and 450 °C (Figures 3b and 3c) exhibited diffraction peaks at 32.18, 36.61, 47.86, and 63.16°, which indicated the presence of the hexagonal phase. The diffraction pattern of the orange material produced at 450 °C (Figure 3d) contained no detectable traces of the hexagonal phase. The X-ray diffraction data obtained for the transported material were analyzed using the Rietveld method (Figure 4). The intensities of the experimental diffraction peaks closely matched those calculated for GaN possessing the zinc blende structure (Figure 4, bottom). The lattice constant of the bulk cubic GaN was refined to a value of 4.506 Å. This value compared well with the lattice constant measured for the cubic portions of the disordered nanocrystals obtained from the solid-state pyrolysis of $[H_2GaNH_2]_3$ (4.50 Å) as well as that measured for thin films of cubic GaN produced by MOCVD and MBE (4.51−4.55 Å).[20−23]

This transported material was also studied by electron microscopy. SEM (Figure 5) indicated that the material crystallized in an arrowhead morphology with the particles ranging in size from several to tens of micrometers. The presence of what appeared to be etch pits was also observed in these images. TEM analysis of an ~1 μm single crystal (Figure 6) revealed that the material was free of defects such as the stacking faults found in the nanocrystalline material. This was supported by the corresponding electron diffraction pattern, which consisted of a set of sharp spots corresponding to the 110 pattern of GaN having the zinc blende structure. In this orientation, two sets of 111 twinning planes are visible, but no stacking faults are observed. EDAX analysis of the same single crystal during the TEM study was unable to detect the presence of iodine down to the detection limit of ~0.1%.

The GaN sample synthesized at 350 °C was also analyzed by TEM. Dark field images of the square particles (normal to the electron beam) revealed a concentric pattern of thickness fringes (Figure 7). The presence of these fringes, and the change in shape of the projection of the particle as it was tilted, suggested that the GaN particles crystallized as tetrahedra. The electron diffraction pattern of one of these crystallites was consistent with the 100 pattern of GaN possessing the zinc blende structure. Most of the crystals grown
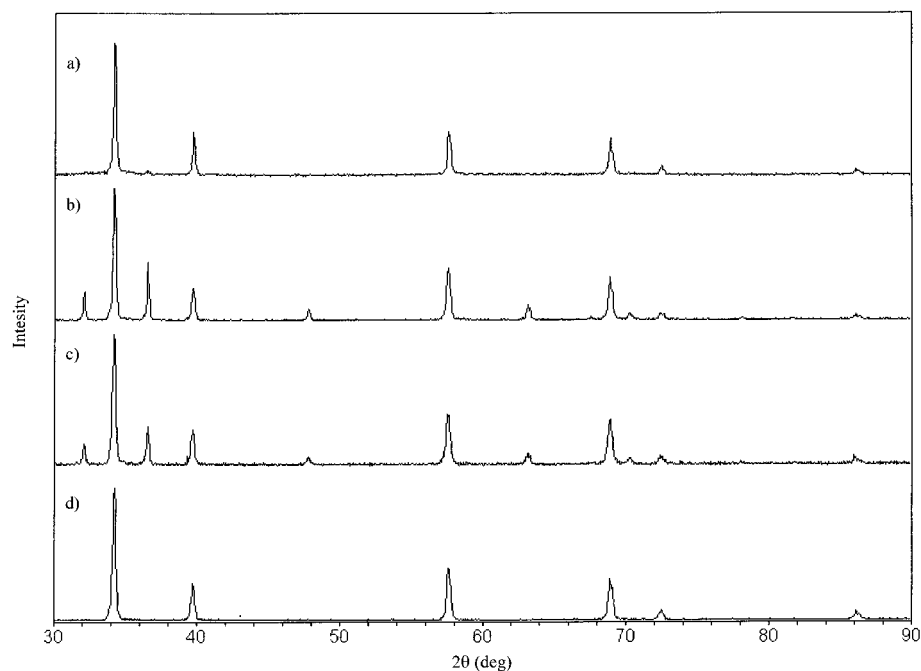
Figure 3. X-ray diffraction patterns of the cubic GaN produced from $[H_2GaNH_2]_3$ and NH_4I emphasizing the effect of reaction temperature on product phase. The diffraction patterns are of the products obtained at (a) 257 °C (cubic), (b) 349 °C (cubic + hexagonal), and (c) 445 °C (cubic + hexagonal), and The diffraction pattern shown in d) is of the cubic material which was transported to the side of the reaction vessel at 445 °C. Peak assignment (°2θ): 32.12 (100, h-GaN), 34.26 (002, h-GaN; 111, c-GaN), 36.61 (101, h-GaN), 39.76 (200, c-GaN), 47.86 (102, h-GaN), 57.65 (110, h-GaN; 220, c-GaN), 63.16 (103, h-GaN), 67.55 (200, h-GaN), 68.89 (112, h-GaN; 311, c-GaN), 70.26 (201 h-GaN), 72.45 (004, h-GaN; 222, c-GaN), 78.12(202, h-GaN), 81.77 (104 h-GaN), 86.15 (400 c-GaN).
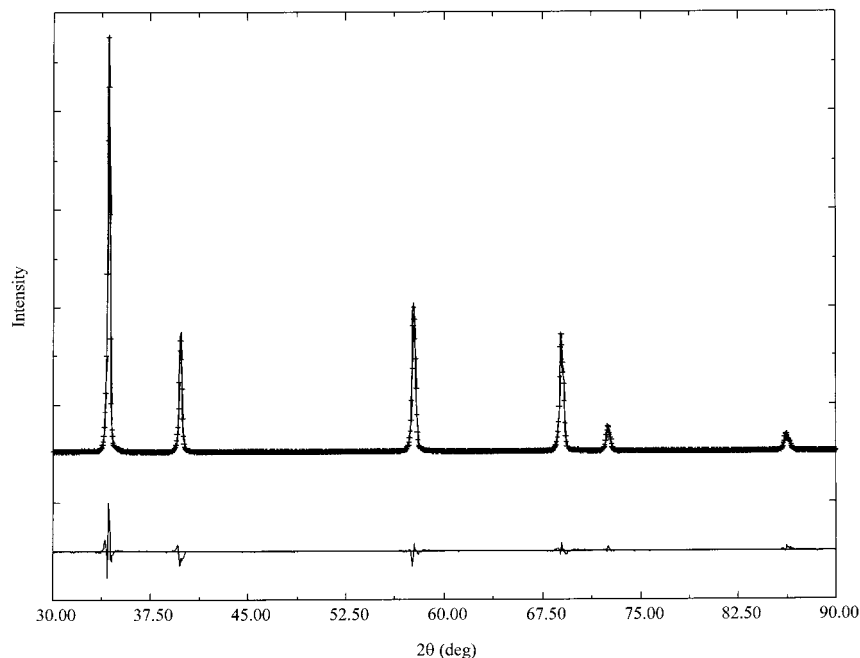
Figure 4. Rietveld refinement of the XRD data of the transported cubic GaN produced from $[H_2GaNH_2]_3$ and NH_4I at 445 °C: (+) experimental pattern, (solid line) refined pattern, (bottom) difference pattern. The lattice constant was refined to a value of $a = 4.506$ Å.

at this temperature were relatively free of defects; several particles did show evidence of the presence of several stacking faults.

Discussion

Ammonothermal Synthesis and Growth of Nanocrystalline GaN. Cyclotrigallazane, $[H_2GaNH_2]_3$, was found to be an effective precursor for the synthesis of

GaN under ammonothermal conditions. The conversion apparently proceeded through the previously reported intermediate poly(imidogallane), $[HGaNH]_n$ (Scheme 1).[34,35] The thermolysis of $[H_2GaNH_2]_3$ in ammonia

(34) Jegier, J. A.; McKernan, S.; Gladfelter, W. L. *Chem. Mater.* **1998**, *10*, 2041.
(35) Jegier, J. A.; McKernan, S.; Gladfelter, W. L. *Inorg. Chem.* **1999**, *38*, 2726.
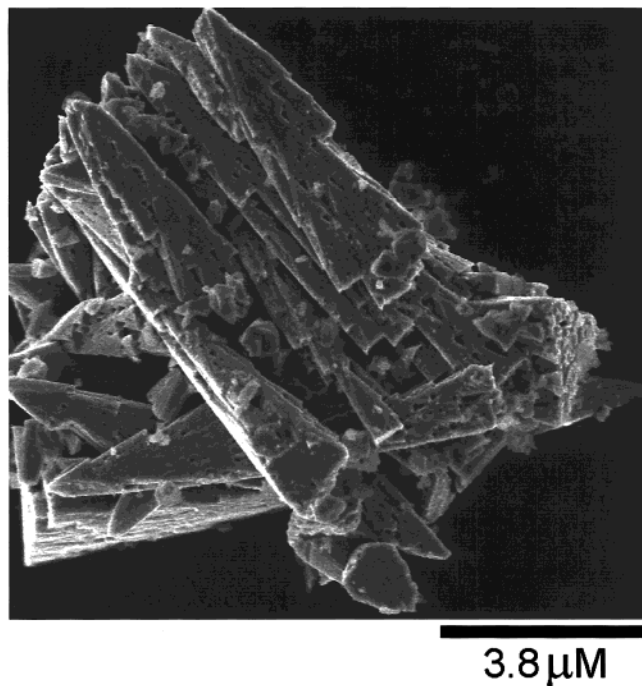
Figure 5. Plan view scanning electron micrograph of the transported cubic GaN produced from $[H_2GaNH_2]_3$ and NH_4I at 445 °C. The surfaces of the crystallites display what appear to be numerous etch pits.

solution led to GaN powders that differed from those obtained in the solid-state pyrolysis of $[H_2GaNH_2]_3$.[5,6] The off-white color of the sample was in contrast with the gray-black $GaN_{0.83}$ powders obtained from solid-state pyrolysis of $[H_2GaNH_2]_3$ at 600 °C. The gray-black color was attributed to gallium enrichment, resulting from the elimination of NH_3 during pyrolysis. The use of NH_3 as a solvent would tend to minimize the ammonia-loss problem. The coherent length of the sample, 3 nm, was also different than that of the nanocrystalline GaN powder obtained from the solid-state pyrolysis of $[H_2GaNH_2]_3$ (6 nm).

While annealing the GaN powder under N_2 at 600 °C for 4 h did not lead to an increase in the coherent length of the sample, it was found that larger crystallites could be obtained in supercritical ammonia by increasing the reaction time or temperature. Conducting the ammonothermal reaction at 200 °C for 5 h or at 150 °C for 24 h produced GaN powders with average coherent lengths of 4 nm. Further increases in temperature led to the isolation of GaN powders with average coherent lengths of 8 nm (250 °C), 14 nm (350 °C), and 17 nm (450 °C). As the $[H_2GaNH_2]_3$ is rapidly consumed at the beginning of these reactions, it is proposed that this increase in coherent length occurs via Ostwald ripening. While crystallite growth through Ostwald ripening is common in the solution-phase syntheses of other semiconductor nanoparticles such as CdS and CdSe,[36] it has been less frequently recognized for compounds such as GaN whose physical properties, including solubility, are more akin to ceramic materials.

Ammonothermal crystal growth of group 13 nitrides, MN (M = Al, Ga), has previously been observed under basic conditions.[27–31] In the case of Al, the reaction of

Al^0 or AlN with KNH_2 in supercritical ammonia led to the production of large AlN crystals. The transport of the insoluble AlN powder involved in forming the large crystals was proposed to be due to the reversible formation of $K[Al(NH_2)_4]$:[31]

$$AlN + KNH_2 + 2NH_3 \rightleftharpoons K[Al(NH_2)_4] \qquad (1)$$
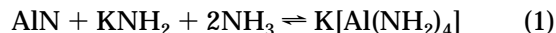
A similar reaction can be proposed for the growth of the GaN nanocrystals. Although no separate source of $[NH_2]^-$ was added, very small concentrations of $[NH_2]^-$ are present due to the autoionization of NH_3. The autoionization constant for NH_3 was reported as 3.2×10^{-33} ($[NH_2]^- = 5.2 \times 10^{-17}$ M) at 240 K.[37] The concentration of $[NH_2]^-$ is expected to increase under the conditions used in this study; the autoionization constant was estimated to be 5.6×10^{-22} ($[NH_2]^- = 2.4 \times 10^{-11}$ M) at 723 K (450 °C). The autoionization of NH_3 also produces $[NH_4]^+$ which, as discussed below, can also promote crystal growth of GaN. While it has previously been shown that bulk GaN is unreactive toward NH_3 under ammonothermal conditions,[29] a higher surface reactivity of the nanocrystals may facilitate such reactions, allowing transport of the material and crystal growth.

Structure of the Nanocrystalline GaN. Modeling of the X-ray intensity data of the GaN obtained from the solid-state pyrolysis of $[H_2GaNH_2]_3$ indicated that the best fit to the experimental pattern consisted of particles with a large number of stacking faults.[6] These stacking faults lead essentially to a random arrangement of cubic and hexagonal close-packed layers and cause those X-ray reflections specific to only one of the phases (e.g., $h00$ for cubic and $10l$ for hexagonal) to disappear. The similarities between the GaN diffraction patterns produced under ammonothermal conditions and those previously reported suggest that the structure of the samples produced under ammonothermal conditions is also composed of a random arrangement of cubic and hexagonal close packed planes.

High-resolution TEM images of the 17-nm (by XRD) particles produced at 450 °C revealed a striped appearance caused by stacking faults. The electron diffraction patterns of the crystallites exhibited streaking of the diffraction spots perpendicular to the close-packed planes; also consistent with a structure containing numerous defects such as stacking faults. While these striations could also be described as micro-twinning,[38] the electron diffraction data and the presence of peaks attributable to both the cubic and hexagonal phases in the X-ray diffraction pattern suggest a disordered structure containing stacking faults.

Synthesis of Cubic GaN in the Presence of NH_4I. The ammonothermal crystal growth of group 13 nitrides under acidic conditions has been reported.[24,27,32] Typically, a mineralizing agent such as NH_4I is reacted with the metal nitride or nitride precursor in supercritical ammonia resulting in an ammonia-soluble species. For instance, the reaction of Al^0 with NH_4I resulted in the formation of $[Al(NH_3)_6]I_3$ which was then converted to

(36) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

(37) Coulter, L. V.; Sinclair, J. R.; Cole, A. G.; Roper, G. C. *J. Am. Chem. Soc.* **1959**, *81*, 2986.

(38) Oktyabrsky, S.; Dovidenko, K.; Sharma, A. K.; Joshkin, V.; Narayan, J. *MRS Internet J. Nitride Semicond. Res.* **1999**, *Res. 4S1*, G6.43.
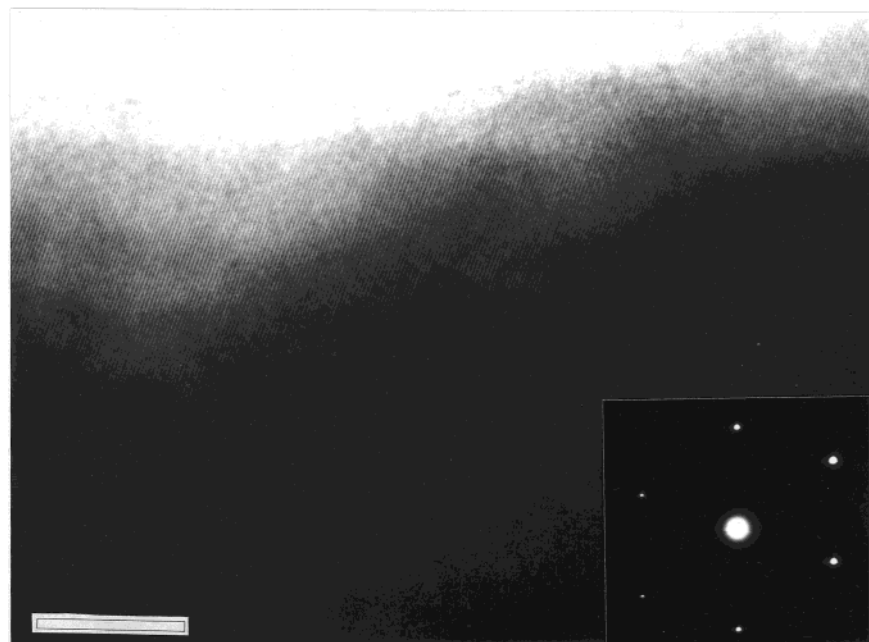
Figure 6. High-resolution transmission electron micrograph and corresponding electron diffraction pattern (110 pattern, inset) of the transported cubic GaN produced from the reaction of $[H_2GaNH_2]_3$ and NH_4I at 445 °C. The observed lattice fringes indicate a well-crystallized material relatively free of defects such as stacking faults. The scale bar represents 10 nm.
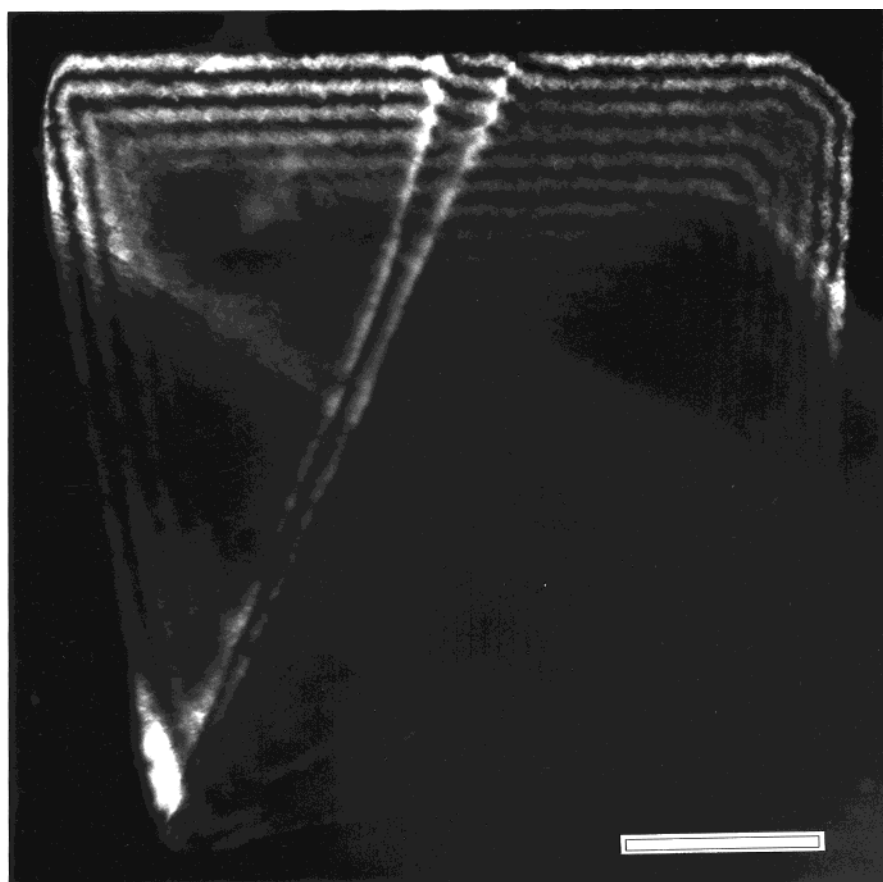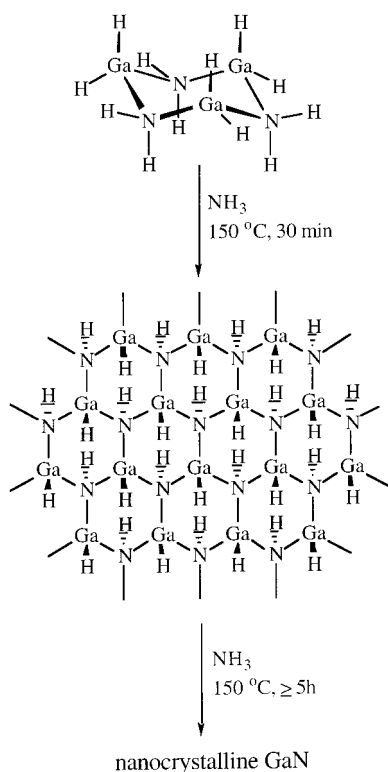

Figure 7. Dark field transmission electron micrograph of the GaN produced from the reaction of $[H_2GaNH_2]_3$ and NH_4I at 349 °C. The crystal is oriented close to the [100] direction. The concentric pattern of thickness fringes establishes that the GaN product crystallizes as tetrahedra. The diagonal lines seen in the image are consistent with dislocations. The scale bar represents 0.1 μm.

$AlN.^{32}$ The synthesis of $AlF_3(NH_3)_2$ from the reaction of AlN and NH_4F in supercritical ammonia serves as another example and illustrates the type of species formed under these conditions.[27] To assess the impact of an acidic mineralizing agent on the ammonothermal
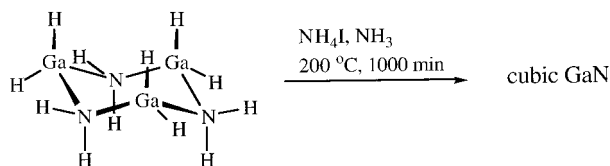
conversion of cyclotrigallazane to GaN, $[H_2GaNH_2]_3$ was reacted with NH_4I (1:1 mass ratio) in supercritical ammonia (Scheme 2). Two important differences were found. Under similar conditions the crystallites were orders of magnitude larger than those grown in the
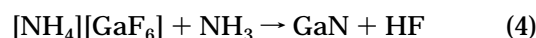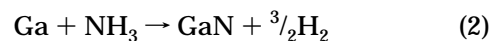
Scheme 1

$$NH_3$$
150 °C, 30 min

$$NH_3$$
150 °C, ≥ 5h

nanocrystalline GaN

Scheme 2

$$NH_4I, NH_3$$
200 °C, 1000 min → cubic GaN

absence of NH₄I, and much or all of the GaN had the zinc blende structure. On the basis of precedent of using [NH₄]⁺ as a mineralizer, the increase in crystallite size was expected; however, the nature of the specific reactions involving [NH₄]⁺ is unknown. The NH₄I could react directly with the cyclotrigallazane to produce a new, soluble growth species. Preliminary studies of the reaction of NH₄I with [H₂GaNH₂]₃ at low temperature (−33 °C) revealed the formation of an uncharacterized hydrido−amido complex of gallium. Further studies will attempt to isolate this species and examine its reactivity. It is also likely that the NH₄I induces grain growth by solubilizing a small fraction of the GaN.

Far more intriguing is the observation that cubic GaN is formed. This adds cyclotrigallazane to a list of several gallium compounds (e.g. Ga⁰, GaI₂, GaI₃, Ga(NH)₃₋ₓ/₂Iₓ, etc.) that also form large crystallites of cubic GaN under ammonothermal conditions in the presence of ammonium salts.[24] That this range of compounds produces a common product suggests that the events leading to crystal growth are the same; however, it offers no clue as to why cubic GaN is formed. We offer the simple

hypothesis that below ~300 °C, the zinc blende structure is the more stable phase of GaN. This would partially explain why the ammonothermal reactions at 200 °C with [H₂GaNH₂]₃/NH₄I and at 300 °C with Ga⁰/NH₄I produced relatively pure cubic GaN, but the same reactions conducted above 320 °C produced mixtures of the cubic and hexagonal phases. However, the deposition of pure cubic GaN in the middle of the tube at an estimated growth temperature of 350−370 °C indicates that this may not be the whole story. For previous experiments with Ga⁰/NH₄I, the extreme dependence of the relative amounts of the cubic and hexagonal phases in the deposited product on the heating program used to attain the final growth temperature strongly suggests that the product mixture is at least partially kinetically determined.[24] The latter would apply particularly to the higher temperatures (>430 °C), where more mineralization and transport occur.

The cubic phase has not been produced by any of the earlier syntheses of bulk powders because these reactions (eqs 2−4[39−41]) were typically run above 900 °C.

$$Ga + NH_3 \rightarrow GaN + {}^3/_2H_2 \qquad (2)$$

$$Ga_2O_3 + 2NH_3 \rightarrow GaN + 3H_2O \qquad (3)$$

$$[NH_4][GaF_6] + NH_3 \rightarrow GaN + HF \qquad (4)$$

Considering the small energy differences between wurtzite and zinc blende GaN, electronic structure calculations estimate the internal energy preference for the wurtzite form as 1. 9 kJ/mol (at $T = 0$ K),[42] it is not surprising that a phase transition might exist at these previously unexplored temperatures.

In summary, supercritical ammonia appears to be a promising media for controlled growth of GaN crystals and nanocrystals. More research is necessary to understand the details of this complex process and to develop methods that will improve control of the dispersion in crystallite size.

Note Added in Proof. The reaction of elemental Ga and N₂ in a Na−Ga melt produces a mixture of hexagonal and cubic GaN (Yamane, H.; Shimada, M.; DiSalvo, F. J. *Mater. Lett.* **2000**, *42*, 66−70).

(39) Johnson, W. C.; Parsons, J. B.; Crew, M. C. *J. Phys. Chem.* **1932**, *36*, 2651.
(40) Schoonmaker, R. C.; Burton, C. E. *Inorg. Synth.* **1963**, *7*, 16.
(41) Juza, R.; Hahn, H. *Z. Anorg. Allg. Chem.* **1940**, *244*, 111.
(42) Yeh, C.-Y.; Lu, Z. W.; Froyen, S.; Zunger, A. *Phys. Rev. B* **1992**, *46*, 10086.