Solvothermal Azide Decomposition Route to GaN Nanoparticles, Nanorods, and Faceted Crystallites

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We report a straightforward, nonaqueous, solvothermal method for the production of nanoscale gallium nitride structures. Nanoparticles with spherical and rodlike morphologies are produced via in situ gallium azide precursor synthesis and decomposition in superheated toluene or THF. The solution reaction between gallium chloride and sodium azide produces an insoluble azide precursor that solvothermally decomposes to GaN at temperatures below 260 °C. The resulting products are poorly crystalline but thermally stable and crystallize to hexagonal GaN upon annealing at 750 °C. Product morphologies include nanoparticles (ca. 50 nm) and nanorods (ca. 300 nm lengths). Upon annealing, the nanoparticles coalesce into larger organized crystalline structures with hexagonal facets.

Introduction

There is increased interest in materials growth and morphological control in the nanoscale regime. It has been known for some time that nanometer scale particles can exhibit size dependent properties distinct from bulk material such as higher energy optical absorption for semiconductors[1] and increased ductility for metal alloys.[2] Chalcogenide semiconductors such as CdS and CdSe are well studied and solution routes to monodisperse nanoparticles have been devised.[1a] In contrast, viable routes to main group nitride nanoparticles are less developed.

Group 13 nitrides are central to a class of light emitting semiconductors that are finding increasingly utility in devices such as transistors,[3] high-intensity blue lasers, and full color displays.[4] The heavier nitrides, GaN (E_g = 3.4 eV) and InN (E_g = 1.9 eV), have useful band gaps in the UV−visible region and form a wide range of solid solutions. Dual-source vapor phase processes, such as deposition using Me_3Ga and NH_3 at 800−1200 °C, are commonly used to grow GaN films.[5] Gallium nitride is thermally unstable and decomposes to the elements before melting (e.g., N_2 vapor pressure is 3 kbar at 1300 °C), which makes it difficult to produce single crystals by high-temperature melt-based synthetic methods.[6] Small GaN crystals have been synthesized from molten gallium and N_2 at 700 °C in an alkali metal flux[7] and nanorod architectures were observed from catalyzed reactions between gallium and NH_3 above 900 °C.[8] An aerosol process between $Ga(NO_3)_3$ and NH_3 near 1100 °C produces submicron faceted GaN crystallites,[9] and a metathesis reaction between $GaCl_3$ and Li_3N/NH_4Cl rapidly produces crystalline GaN powders.[10]

There has been a significant amount of work on single-source molecular precursors to GaN films and bulk solids where product growth temperatures are usually well below 700 °C. Selected examples of single-source precursors for film growth include amides $[Ga(NMe_2)_3$,[11] $(Et_2GaNH_2)_3$[12]] and azides $[H_2GaN_3$,[13] Cl_2GaN_3,[14] $(Me_2GaN_3)_n$[15]]. The solid-state pyrolysis of polymeric gallium amides, such as $[Ga(NH)_{3/2}]_n$[16] and $(H_2GaNH_2)_n$,[17] produce GaN powders at low temperatures. Of relevance to the present work, a thermally unstable triethylamine adduct of gallium triazide $[Et_3N\cdot Ga(N_3)_3]$ has been shown to rapidly decompose to form GaN nanoparticles.[18]

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Although high-temperature solution reactions are well-developed for water-based (hydrothermal) syntheses, there is much less work on nonaqueous synthetic systems. Recently, organic solvents, sometimes with coordinating character, have been utilized in the solvothermal synthesis of complex chalcogenide structures[19] and semiconductor nanomaterials.[20] Other examples include Si nanocrystal growth from superheated hexane[21] and the catalyzed solvothermal growth of 13−15 nanorods.[22] Solution routes to metal nitrides are much less prevalent than those for chalcogenides or pnictides, however there is a recent report of InN nanorod structures from the solvothermal decomposition of $(^tBu_2InN_3)_n$.[23] Some promising routes include GaN nanoparticles from $GaCl_3$ and Li_3N in superheated benzene,[24] GaN crystals and nanocrystallites from the reaction of gallium or gallium amides in supercritical NH_3,[25] and GaN nanoparticles from the rapid decomposition of gallium azides and amides in hot solvents (ca. 200 °C).[18b,26]

Alkali metal azides have been successfully used as a nitrogen source in metal nitride synthesis[7,27] and azides are attractive as a GaN precursor component because they contain no extraneous Ga−C, N−H, or C−N bonds that must be broken prior to product formation. Due to the thermal instability of many molecular azides, we examined the in situ formation and decomposition of gallium azides in superheated organic solvents. In this paper, we report a one-pot method that results in the synthesis of GaN nanostructures including nanoparticles and nanorods, which grow into larger faceted crystallites upon moderate annealing.

Experimental Section

GaN Solvothermal Reactions. Toluene and THF were dried over sodium or potassium and distilled prior to use. Commercial GaN powder (Aldrich 99.99%) was utilized for comparison purposes. A high-temperature, high-pressure stainless steel reactor (Parr Instruments: 71 mL model 4740 or 125 mL model 4752) was loaded in an argon-filled glovebox with $GaCl_3$ (3.0 g, 17.0 mmol, Aldrich, 99.9%) and NaN_3 (3.3 g, 51.1 mmol, Aldrich, 99.99%). Toluene or THF (75% reactor fill) was added to the reactor, which was then pressurized with one atm N_2. In some cases, NEt_3 or NH_4Cl were added (1−5 mol % relative to $GaCl_3$) to examine their influence as secondary nitrogen sources or catalysts. The sealed reactor was placed in a vertical tube furnace (Thermolyne Model 21110) or custom heating mantle (Glas-Col with an Omega CN4800 temperature controller) and slowly heated. A typical heating regimen for a toluene reaction was 100−125 °C (1 day), 175 °C (1 day), 220 °C (1 day), 260 °C (2−4 days). The preceding temperatures were measured by an internal reactor thermocouple. The maximum reaction temperature was determined as the point where gas evolution ceased, as tracked by the reactor's analogue pressure gauge, which indicated that all of the gallium azide had decomposed. Reaction solutions were removed under inert conditions using cannula techniques and the as-synthesized solids were washed with clean solvent, dried under vacuum overnight, and transferred to an argon-filled glovebox. Reactions performed in THF were run under similar conditions, however a constant pressure was achieved by 220 °C. The NaCl byproduct was removed from as-synthesized samples by dissolution with water or a glycerol/ethanol (75/25 by vol.) solution, followed by vacuum filtration and rinsing with ethanol and diethyl ether. Note that recent experiments show that a more dilute glycerol/ethanol solution (25/75) is equally effective at removing NaCl and is much easier to filter. Selected as-synthesized and washed products were annealed at elevated temperatures (500−1000 °C) in sealed, evacuated silica ampules (2−4 days).

Safety note: Metal azides are often thermally unstable and shock sensitive. Care should be taken whenever working with reactions that may produce azides as products or intermediates. Reactions should be performed on a small scale in high-pressure vessels with safety release valves. Use proper protection when working with undecomposed azide intermediates.

Product Characterization. Solution ^1H and ^{13}C NMR were performed in C_6D_6 on a Bruker AC300 MHz spectrometer. The phase and crystallinity of the products were analyzed by powder X-ray diffraction using a Siemens D5000 diffractometer. A crystalline silicon standard (Alfa-Aesar, 99.9985%, 1−20 μm) and 0.05 degree increments were used for lattice parameter calculations and crystallite size measurements. Lattice parameters were determined by least squares refinement and average crystallite sizes were calculated using the Scherrer and Warren equations relative to the crystalline Si (111) peak.[28] The average size for crystalline GaN was derived from (100) and (101) peak widths and the (110) peak was used for as-synthesized GaN. Infrared spectra were taken on a Nicolet Nexus 670 spectrometer in transmission mode using KBr pellets. UV−visible spectra were obtained from powders suspended in ethanol or methanol solutions using an HP 8453 diode array system. Luminescence measurements were performed on ethanol or methanol suspensions with a Shimadzu RF-1501 spectrofluorophotometer with 250 or 265 nm excitation. Thermogravimetric-differential thermal analysis was run on a Seiko Exstar 6300 system under argon or 20% oxygen flow with a 5 or 10 °C/min heating ramp. Scanning electron microscopy was executed with a Hitachi S-4000 field emission system on powders adhered to aluminum holders. This system included a Kevex elemental X-ray detector for energy dispersive spectroscopy. Transmission electron microscopy was performed on alcohol-dispersed powders on coated Cu grids using a Hitachi H-600 STEM system operating at 100 kV. Bulk elemental analysis was obtained from Desert Analytics (www.desertanalytics.com).

Results and Discussion

In situ GaN Precursor Formation and Decomposition. In the present work, we explored the utility of in situ gallium azide formation and decomposition in a nonaqueous solvothermal environment. Reactions were salt-balanced to yield three moles of NaCl for every

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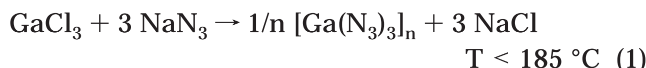
mole of gallium chloride used (eq 1)



$$GaCl_3 + 3\ NaN_3 \rightarrow 1/n\ [Ga(N_3)_3]_n + 3\ NaCl \quad T < 185\ °C \quad (1)$$

The metathesis reaction forming a gallium azide intermediate takes place at moderate temperatures and only pressure rises due to the solvent were evident up to 220 °C (internal temperature) using toluene or up to 185 °C using THF. When the gallium azide precursor and the NaCl byproduct were solvothermally heated to higher temperatures a significant increase in pressure was observed. This pressure rise marks the beginning of gallium azide decomposition. Reaction temperatures were raised until gas evolution ceased, corresponding to 260 °C for toluene and 220 °C for THF (eq 2)

$$[Ga(N_3)_3]_n \rightarrow n\, GaN + 4n\, N_2 \quad (2)$$

Both solvents were utilized near their critical points; however, the onset of gas evolution and decomposition is significantly below the supercritical fluid temperatures for THF (267 °C) and toluene (319 °C).[29] Note that NaN_3 by itself does not decompose in toluene under the conditions used in this study. The filtered solutions after the reaction are orange-brown in color, however ^1H and ^{13}C NMR detected no significant species other than the solvent and the IR and UV-VIS spectra showed no absorption events except those of the solvent; notably, no soluble azides were present. In one reaction, THF (C_4H_8O) was utilized above its critical temperature and the product contained significant amounts of crystalline Ga_2O_3, indicating that reaction with the solvent can occur.

Crystallinity and Thermal Processing. The solvothermal products are brown colored from toluene and tan colored from THF. The crystalline NaCl byproduct was removed before or after annealing. Salt removal was accomplished either by rapid vacuum filtration using water or by washing with a glycerol/ethanol mixture. Both were effective at removing NaCl as determined by powder X-ray diffraction (XRD) and energy dispersive analysis (EDS). Because prolonged water exposure converts GaN to gallium oxide hydrates, glycerol/ethanol was most often utilized. In practice, it was preferable to remove the salt before annealing to avoid its reaction with the silica ampule; however, the salt will transport to cooler regions of the ampule during annealing.

The washed gallium azide toluene decomposition product consists of poorly crystalline GaN with diffuse diffraction corresponding to hexagonal gallium nitride (h-GaN, Figure 1a). The approximate crystallite size is less than 3 nm based on XRD peak broadening. Annealing this material at 750 °C produces 8 nm nanocrystalline h-GaN (Figure 1b) and heating to 1000 °C significantly improves crystallite size to 37 nm (Figure 1c). The lattice parameters for the crystalline hexagonal GaN [a = 3.188(1) Å, c = 5.178(1) Å] agree with literature values.[4,6] Unwashed samples were generally more crystalline (ca. 50% larger sizes) after annealing than washed ones, likely due to the assistance of the

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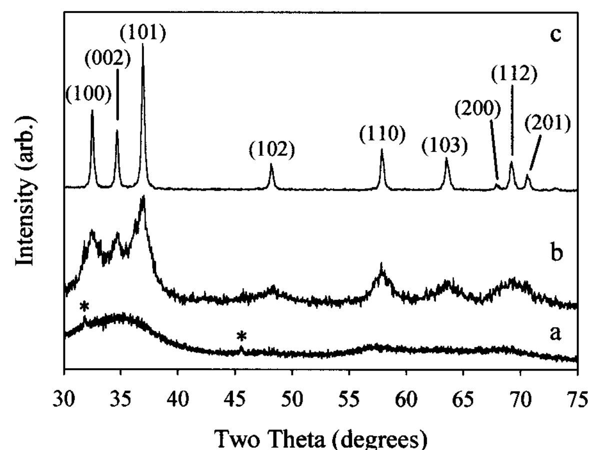

Figure 1. Powder X-ray diffraction of GaN from the reaction of $GaCl_3$ and NaN_3 in superheated toluene washed with glycerol/ethanol to remove NaCl (a), then annealed at 750 °C for 2 days (b), or annealed at 1000 °C for 2 days (c). Hexagonal GaN reflections are labeled with (*hkl*) values and residual NaCl is noted by an *.

molten halide salt flux. Samples from THF reactions exhibit crystallization behavior similar to those from the toluene reactions.

Infrared and Thermal Analysis. A prominent, broad IR absorption centered near 570 cm^{-1} is present in all GaN solvothermal products and corresponds to A_1 and E_1 transverse optical lattice phonon modes of gallium nitride (Figures 2a,b).[30] This absorption region is a useful diagnostic, since it is distinct from Ga−O impurity bands at 650 and 480 cm^{-1}. A recent theoretical study suggests that amorphous GaN materials will exhibit major IR absorptions similar to those of crystalline GaN.[31] The as-synthesized and glycerol/ethanol washed samples show evidence of azides (2100 and 1300 cm^{-1}) and organic residues such as C−C and C−H near 1500 and 1000 cm^{-1}, respectively, which may originate from covalently bound azido, tolyl, or glycerol surface groups. Far IR analysis also shows some absorption consistent with bridging and terminal Ga−Cl groups. Upon annealing only a broad GaN lattice vibration is evident (Figure 2c).

Simultaneous thermogravimetric-differential thermal analysis (TG-DTA) of the as-synthesized product reveals that there are few volatile or decomposable components (Figure 3a). The small (<10%) exothermic loss near 320 °C is attributed to the elimination of surface capping groups and there are no significant other events until NaCl melts and volatilizes above 800 °C. The salt weight loss corresponds to 97% of that expected from a 1:3 molar mixture of GaN and NaCl. The argon TG-DTA of glycerol/ethanol washed GaN also shows surface group loss near 320 °C (Figure 3b). The bulk elemental analysis of a washed GaN sample showed a high nitrogen content and low residual chlorine.[32] The gallium content was determined by a TGA oxidative conversion to Ga_2O_3 at 1000 °C. The N/Ga ratio is consistently near unity by these two measurements. Carbon and hydrogen levels are variable depending on

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(32) GaN elem. anal. wt % (calc. for GaN): C 10.56 (0), H 2.33 (0), N 9.82 (16.7), Cl 1.01 (0), Ga (by TGA) 53.6 (83.3). N/Ga = 0.91.

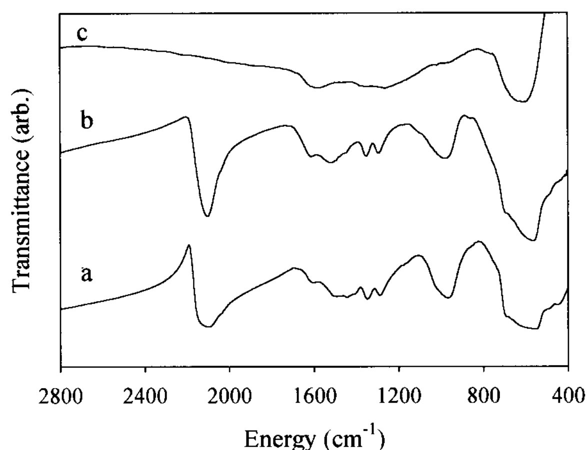


Figure 2. Transmission infrared spectroscopy of GaN from the reaction of $GaCl_3$ and NaN_3 in superheated toluene as-synthesized (a), after washing with glycerol/ethanol (b), and after annealing at 1000 °C (c).

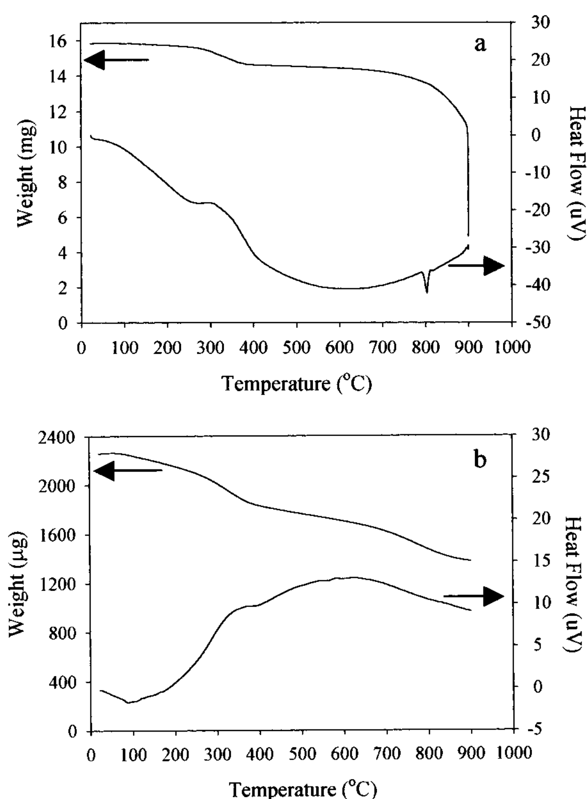
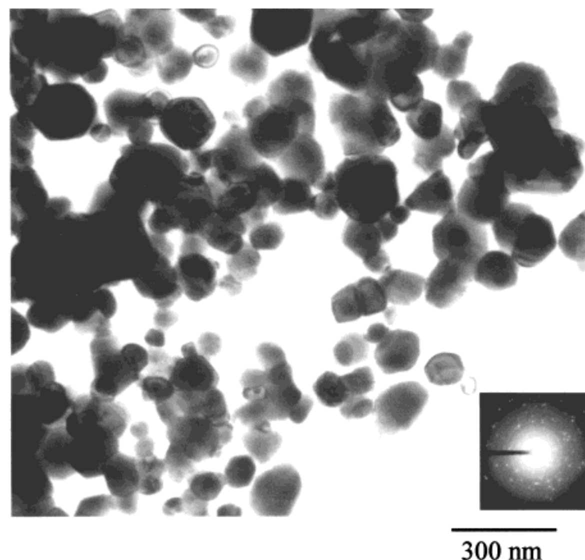
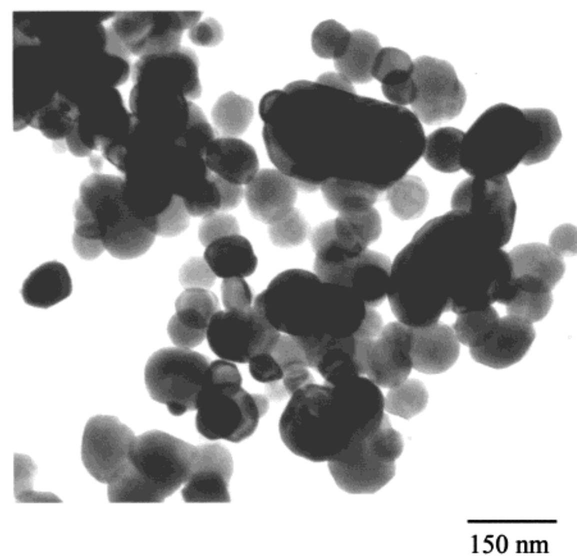


Figure 3. Thermogravimetric-differential thermal analysis (argon, 10 °C/min) on GaN materials isolated from a solvothermal toluene reaction as-synthesized (a) and glycerol/ethanol washed (b). Sample (a) was isothermally heated at 900 °C for 2 h after the ramp.





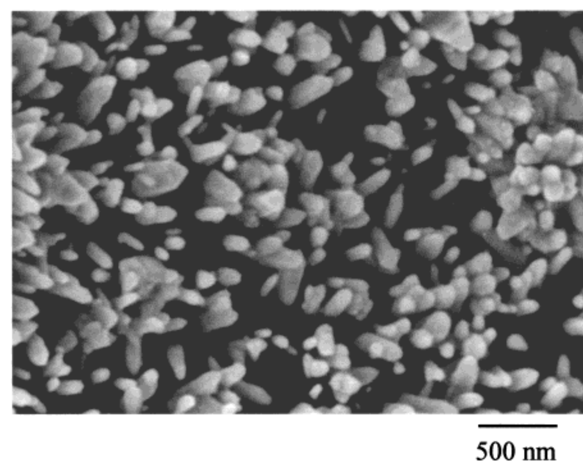


Figure 4. Transmission and scanning electron microscopic images for GaN nanoparticles synthesized from toluene then annealed at 1000 °C (top), or annealed at 1000 °C then washed with water (middle), or washed with glycerol/ethanol then annealed at 1000 °C (bottom). An electron diffraction pattern is shown in Figure 4 (top) inset.

washing regimen and decrease if adherent glycerol is aggressively rinsed away.

Annealed toluene reaction products have a gray color suggesting some surface carbon coating. Selective oxidation (650 °C TGA with 20% O_2) demonstrates that the oxidizable surface carbon is generally less than 10 wt %. Because no gallium oxide is observed by IR or XRD after selective oxidation, it is likely that the GaN crystallites grow carbon coatings from toluene or adherent glycerol residues during annealing. For example, a 40 nm spherical GaN particle would only need a coating of four graphitic carbon layers to account for the observed 10% carbon mass. Bulk elemental analysis of a selectively oxidized sample shows that carbon and hydrogen levels are below 0.3 and 0.1 wt %, respectively.

An indirect nitrogen analysis (TGA, 20% O_2) was performed by converting carbon-cleaned annealed GaN to Ga_2O_3 at 1000 °C and resulted in a weight gains consistent with N/Ga ≥ 1.[33] The nitrogen percentage was calculated assuming the sample was GaN_x after carbon removal. In addition, semiquantitative EDS analysis of annealed samples routinely yielded Ga:N ratios near 50:50.

Nanoscale Morphologies. The product particle sizes from gallium azide decomposition in superheated toluene are generally in the sub 50 nm regime, but micron-sized monoliths are also sometimes observed by electron microscopy. One common morphological feature in these solvothermal GaN reactions is that after annealing, well-formed crystalline nanoparticles are observed. Samples annealed along with the byproduct NaCl have crystallites with hexagonal facets (Figure 4 top), however washing with water smoothes out nanocrystal edges and decreases the particle size somewhat (Figure 4 middle). This is not surprising because bulk GaN is hydrolytically sensitive. The electron diffraction of annealed nanoparticles shows that they are crystalline with the hexagonal wurtzite GaN structure.

In contrast, when salt removal *precedes* high-temperature annealing, the GaN particles are in more intimate contact and grow into larger organized structures such as faceted hexagonal GaN crystallites (Figure 4 bottom). We also occasionally detect flat, micron-sized hexagonal plates from water-washed annealed samples. These plates have crystalline GaN electron diffraction, but GaO_xH_y is also evident by XRD.

Rodlike structures are also observed from solvothermal GaN growth in toluene. These rods are embedded in a salt and nanoparticle matrix, however, after annealing they are clearly resolved (Figure 5 top). Washing annealed samples with water produces smaller, segmented nanorods (Figure 5 middle, bottom). Note that spherical nanoparticles are also present as usual.

The GaN products from solvothermal THF reactions have properties similar to those of toluene; however, the washed material exhibits a more highly interconnected network of nanoparticles (Figure 6 top). Because THF will dissolve the NaCl byproduct *during* the solvothermal reaction, a more intimate level of GaN particle contact and fusion occurs in THF. Large (>10 μm) cubes of NaCl are observed in the as-synthesized material suggesting that the salt is recrystallized from hot THF. After salt removal and annealing, the GaN particles show a high propensity toward faceted hexagonal plate-like crystal growth (Figure 6 middle, bottom). Scheme 1 is a pictorial summary of the solvothermal decomposition process and the observed effect of the salt matrix on annealed product morphologies.

Optical Properties. Gallium nitride exhibits luminescence in the near UV region of the spectrum (365 nm or 3.4 eV) when excited with high-energy radiation. Figure 7a shows photoluminescence from methanol suspensions of washed GaN particles from toluene and THF reactions. The major emission events reveal that surface coatings may overshadow the intrinsic GaN emission. For reference, toluene strongly emits at 280 nm and THF weakly emits at 282 nm. The observed high energy (320 nm) and low energy (425 nm) major emissions are attributed to surface species; however, both curves have distinct shoulders in the 360−380 nm region (3.45 eV − 3.27 eV) consistent with GaN. The UV−vis absorption spectrum of toluene-synthesized

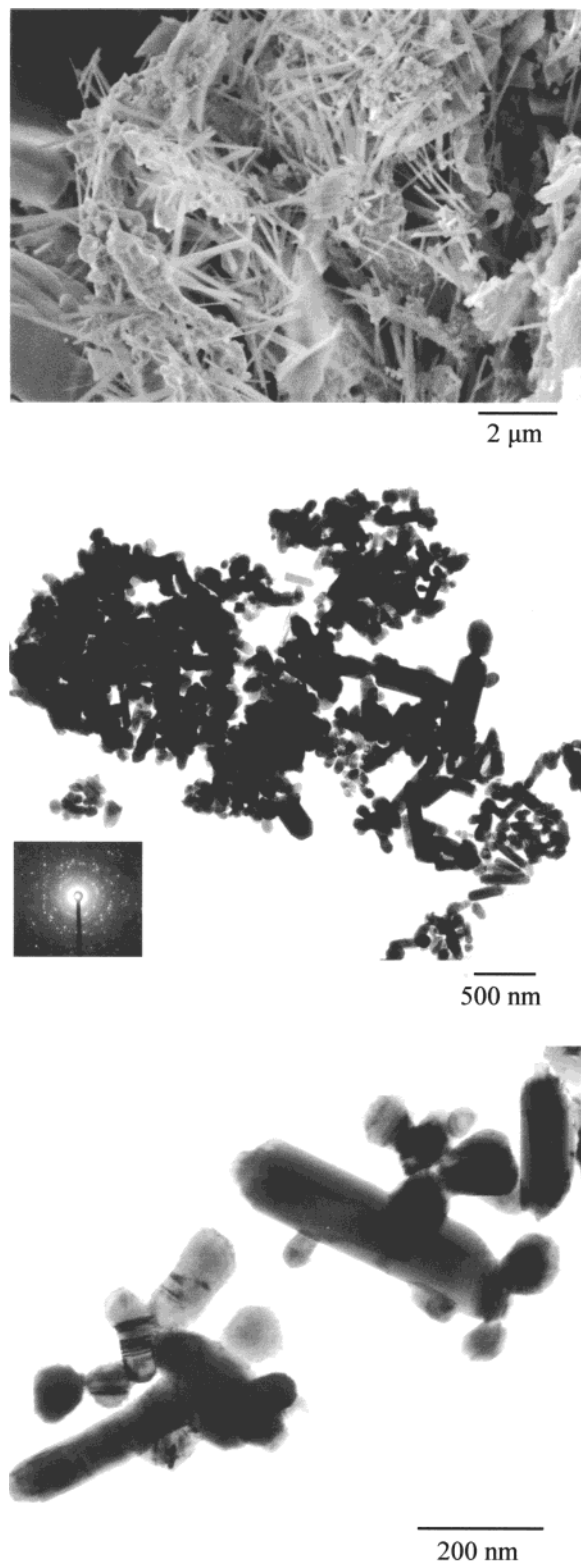


Figure 5. Transmission and scanning electron microscopic images for GaN nanorods synthesized from toluene and washed briefly with glycerol/ethanol (partial NaCl removal) then annealed at 1000 °C (top), followed by a water wash (middle and bottom). An electron diffraction pattern is shown in Figure 5 (middle) inset.

(33) TGA oxidation wt % (wt % by EA): toluene rxn − Ga 73.8, N 17.5 (12.2); THF rxn − Ga 57.5, N 13.9 (11.4).

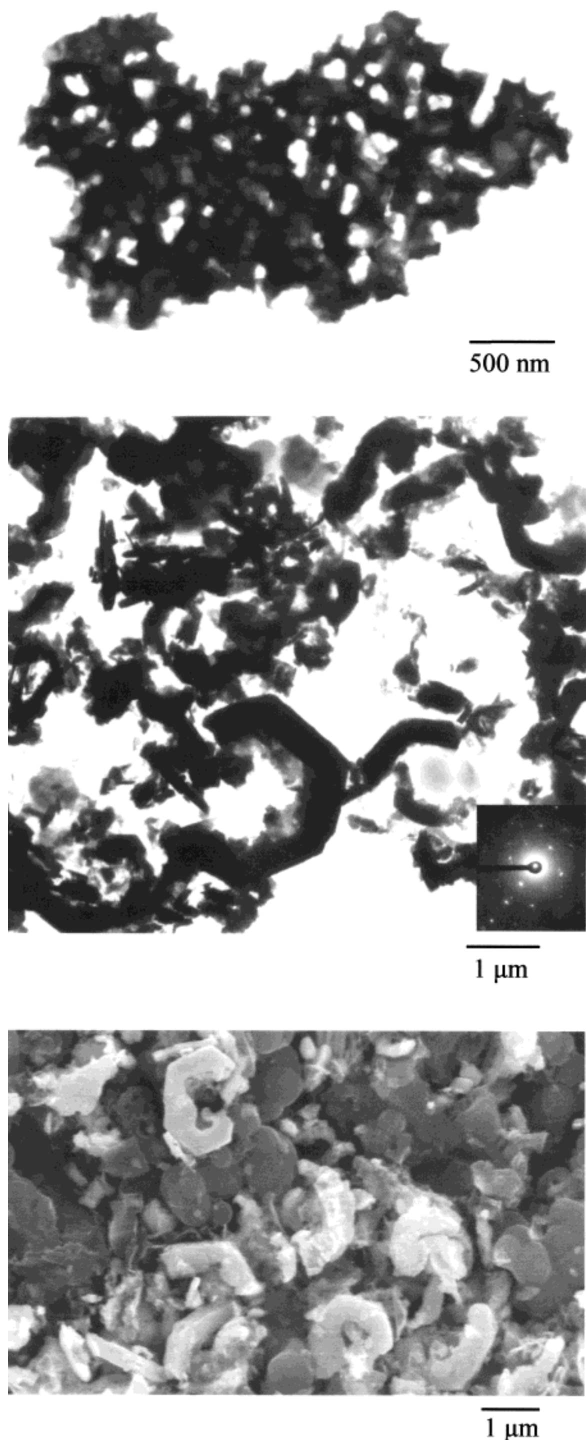


Figure 6. Transmission and scanning electron microscopic images for GaN materials grown from superheated THF and washed with glycerol/ethanol (top), then annealed at 1000 °C (middle and bottom). An electron diffraction pattern is shown in Figure 6 (middle) inset.

gallium nitride material shows broad absorptions in the 290 and 360 nm regions.

Annealed GaN nanocrystals exhibit emission comparable to that of commercial GaN, including band gap emission and impurity states (Figure 7b).[34] The commercial GaN has a 20 nm average crystallite size. The emission at 470 nm appears to be related to surface oxidation because partially oxidized GaN shows a

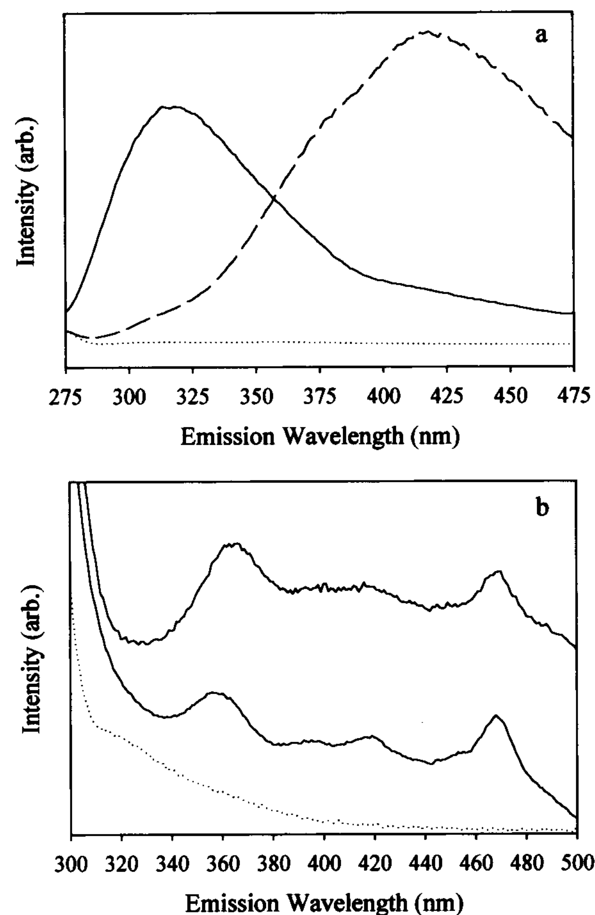


Figure 7. (a) Luminescence measurements (250 nm excitation) on methanol suspensions of glycerol/ethanol washed GaN products from toluene (solid) and THF (dashed) reactions. (b) Luminescence measurements (265 nm excitation) on ethanol suspensions of annealed GaN from a toluene reaction (top curve) and crystalline GaN from commercial sources (middle curve). On each graph, a blank alcohol spectrum is included for reference (lower dotted curves).

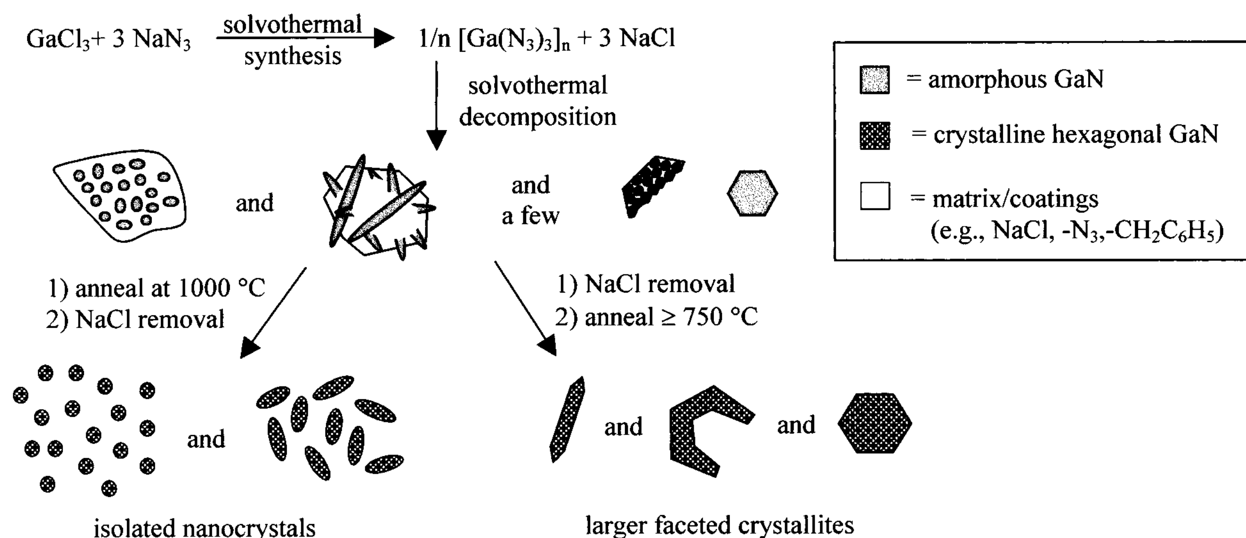
stronger 470 emission and a correspondingly decreased 365 nm emission. Note that solution photoluminescence measurements require particle suspension and the band gap emission near 365 nm sometimes shifts slightly to higher energy as the larger crystals settle out leaving smaller nanocrystallites in solution.

Potential Decomposition Pathways. Low-temperature reactions between $GaCl_3$ and NaN_3 in THF produce either $NaGa(N_3)_4$ or polymeric $[Ga(N_3)_3]_n$ species,[35] which are precursors to amine stabilized $Ga(N_3)_3$ that rapidly produces GaN upon evacuation or injection into hot triglyme (216 °C).[18] The decomposition of $NaGa(N_3)_4$ in the solid state is reported to occur near 150 °C.[35b] At this stage we cannot rule out the intermediate formation of $NaGa(N_3)_4$ or $[Cl_xGa(N_3)_{3-x}]_n$ polymers in our solvothermal reactions. When the toluene solvothermal reaction was stopped *prior* to gas evolution (175 °C), the resulting brown solid only shows crystalline NaCl by XRD and has a strong azide infrared signature at 2105 cm^{-1}. The argon TG-DTA of this solid reveals that a rapid and exothermic decomposition event

(34) Strite, S.; Morkoc, H. *J. Vac. Soc. Technol. B.* **1992**, *10*, 1237.

(35) (a) Fischer, R. A.; Mieher, A.; Herdtweck, E.; Mattner, M. R.; Ambacher, O.; Metzger, T.; Born, E.; Weinkauf, S.; Pulham, C. R.; Parsons, S. *Chem. Eur. J.* **1996**, *2*, 1353. (b) Sussek, H.; Stowasser, F.; Pritzkow, H.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2000**, 455.

Scheme 1. Summary of Solvothermal GaN Growth and Morphological Variations



occurs between 285 and 300 °C. The thermal characteristics of this amorphous azide are comparable with those reported for $[Ga(N_3)_3]_n$.[35] On the basis of previous work one might expect that THF or Et_3N may extract soluble gallium azides and result in lower decomposition temperatures in solvothermal reactions. In THF, azide decomposition occurs approximately 40 °C lower than in the toluene, however the resulting product is qualitatively similar. The addition of Et_3N produced no identifiable changes in the decomposition temperature or product morphology. The addition of NH_4Cl to the toluene reaction also had no quantifiable effect on the decomposition process or GaN product properties. We are continuing to investigate the effect of solvent and additives on the decomposition and nanocrystalline growth process and are attempting the separation and isolation of crystalline GaN nanoparticles through post-reaction processing.

Conclusions

The solvothermal reaction between gallium chloride and sodium azide results in an azide precursor that decomposes to amorphous/nanocrystalline GaN at temperatures at or below 260 °C. Both toluene and THF were utilized as superheated solvents near their critical points and produce gallium nitride materials and a NaCl byproduct. The as-synthesized materials contain strong signatures for nanocrystalline GaN with organic surface coatings. Because THF has a larger propensity to solubilize NaCl during the solvothermal reaction, it results in a more highly agglomerated product. The azide reagent provides all of the nitrogen necessary for the formation of GaN and no other nitrogen sources are necessary during annealing. The GaN morphologies include nanocrystalline particles and rods and faceted crystallites, depending on whether NaCl is removed before or after annealing. Upon annealing, the agglomerated THF products coalesce into larger, organized, hexagonally faceted structures.

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