

## Room-Temperature Synthesis of GaN Nanopowder

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Simple and convenient synthetic routes to GaN are needed for preparing both nanostructured and bulk forms of this important semiconductor. Here, we report a procedure that produces GaN nanoparticles in high yield at ambient pressure and room temperature. The method is based on the metathesis reaction between lithium nitride and gallium halides that has been widely studied by others.<sup>1–6</sup> We have recently discovered that diethyl ether greatly accelerates the reaction between GaCl<sub>3</sub> and Li<sub>3</sub>N so that it proceeds at a measurable rate even at room temperature. In addition to speeding up the reaction, the ether also regulates the reaction temperature, which is important for this highly exothermic process. This new, scalable method appears to be the safest and most practical reported to date for the production of GaN powders. Spectroscopic data show evidence for excitonic quantum confinement in the unannealed product.

As mentioned above, the production of GaN via metathesis reactions between lithium nitride and gallium halides has been studied extensively.<sup>1–6</sup> The appeal of these reactions stems in part from the relatively innocuous reactants and strong driving force for these reactions. Because these reactions are highly exothermic, they occur rapidly and spontaneously once the process has been initiated. This high exothermicity, however, represents a serious drawback because the high temperatures attained lead to spontaneous decomposition of the product into elemental Ga and N<sub>2</sub>.

Kaner and co-workers studied the solid-state metathesis reaction between GaI<sub>3</sub> and Li<sub>3</sub>N.<sup>1–3</sup> By applying high pressure (4.5 GPa), these workers were able to suppress the evolution of N<sub>2</sub> gas and obtain the GaN product in 87% yield.<sup>1</sup> In subsequent work, this reaction was performed in the presence of NH<sub>4</sub>Cl and/or LiNH<sub>2</sub> additives. Although these additives served as an effective heat sink, they also significantly reduced the reaction yield.<sup>2,3</sup>

The metathesis reaction has also been conducted in an organic solvent. Xie and co-workers studied the reaction of

GaCl<sub>3</sub> with Li<sub>3</sub>N in benzene near its critical point.<sup>4,5</sup> After 6–12 h, dark gray, nanocrystalline GaN powder was recovered. In another study, Wells and Janik studied the reaction between GaBr<sub>3</sub> and Li<sub>3</sub>N in refluxing diglyme and xylene.<sup>6</sup> The product obtained after 80 h reaction in this solvent mixture was a powder highly enriched in gallium.

Other researchers have demonstrated that thermal decomposition of gallium azide can produce GaN in high yield.<sup>7–10</sup> Like the aforementioned metathesis, the azide decomposition is difficult to control. Moreover, the metal azides represent a significant hazard, because they are thermally unstable, shock-sensitive explosives.

In the present work, GaN was synthesized by combining Li<sub>3</sub>N and GaCl<sub>3</sub> in a 1:1 mixture of benzene and ether or in pure ether (see the Supporting Information for details). At room temperature, this reaction is exceedingly slow in pure benzene and most other solvents. After 2 days, the starting materials were not noticeably changed in benzene alone. The addition of ether greatly accelerated the reaction so that it was complete within hours at room temperature.

Powder X-ray diffraction (XRD) measurements (Figure 1) on the unannealed powders revealed two broad peaks centered at 35 and 62°. These broad, featureless peaks are typical of nanosized domains, and the diffraction pattern qualitatively matched those obtained by other workers from nanocrystalline GaN.<sup>1,6,9,10</sup> High-temperature annealing of the product under a vacuum or argon yielded narrower peaks that permitted unambiguous identification of the powder as GaN. The progression of the annealing of the products obtained from benzene/ether and from pure ether were qualitatively similar, though the pure ether samples tended to have higher proportions of zinc blende phase throughout the anneal. Three-hour anneals produced mixed phases, with higher temperature favoring a higher wurtzite fraction. Annealing at 850 °C produced almost exclusively wurtzite phase. In contrast, a 5 min flame anneal under argon yielded primarily the metastable zinc blende phase with little wurtzite phase present (note the absence of features at 36 and 64° in the flame anneal pattern). This study demonstrates the feasibility of selecting the desired phase through reaction and annealing conditions. At high temperatures, annealing initially produces zinc blende GaN, but continued annealing is accompanied by a slow cubic-to-hexagonal phase transition.

Raman spectra of the GaN powders were collected using nonresonance excitation at 532 nm. Figure 2 shows the spectrum of (a) the as-prepared sample, (b) a sample annealed at 310 °C, and (c) a commercially obtained 99.99% GaN powder. The as-prepared powder exhibits an intense peak at 713 cm<sup>-1</sup>, accompanied by a shoulder on the low-energy side and a broad hump near 300 cm<sup>-1</sup>. Upon annealing, the

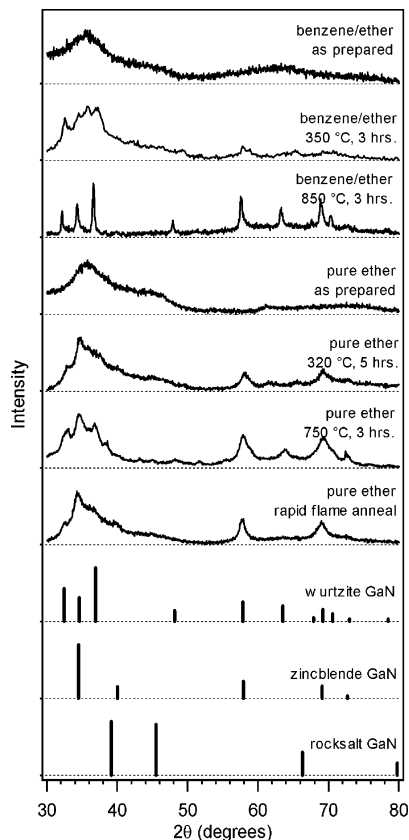
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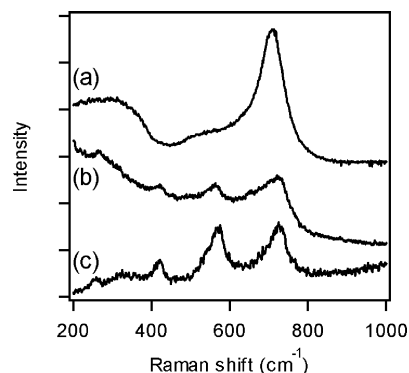
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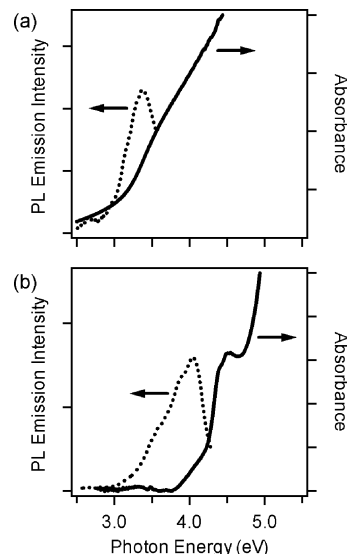
**Figure 1.** XRD study of GaN nanopowders prepared at room temperature in benzene/ether or in pure ether. Annealing conditions are indicated above curves. Diffraction patterns for wurtzite, zinc blende, and rocksalt GaN phases are shown at the bottom of the figure.



**Figure 2.** Raman spectra of (a) as-prepared GaN nanopowder, (b) GaN nanopowder after 3 h anneal at 300 °C, and (c) commercially obtained 99.99% GaN powder.

peak at  $713\text{ cm}^{-1}$  shifts  $\sim 20\text{ cm}^{-1}$  higher and the shoulder narrows into a distinct peak near  $570\text{ cm}^{-1}$ . Although the peaks in curve b remain broad (because of small crystallite size and some remaining disorder), the four main features can all be assigned to known GaN modes. The peak at  $730\text{ cm}^{-1}$  is the longitudinal  $A_1$  mode, and the peak at  $570\text{ cm}^{-1}$  contains contributions from both the transverse  $E_1$  mode and the high frequency  $E_2$  mode. Finally, the two peaks near  $250$  and  $420\text{ cm}^{-1}$  are ascribed to a zone boundary phonon and acoustic overtones, respectively, in accordance with previous assignments.<sup>11–14</sup>

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**Figure 3.** Optical spectra of GaN nanopowders. Graphs show UV absorption spectra (solid curves) and PL emission spectra (dotted curves) of (a) annealed GaN nanopowder and (b) as-prepared GaN nanopowder.

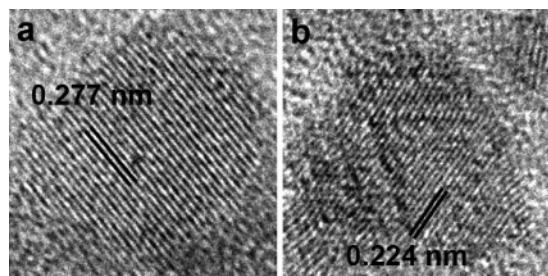
The annealed samples are readily identified as GaN from their XRD patterns. The identity of the unannealed sample is less obvious because of the lack of sharp diffraction peaks. We rely on several pieces of evidence to assign the unannealed product as GaN. First, this metathesis reaction is not known to produce products other than GaN and LiCl. Indeed, LiCl is the only byproduct detected, and its identity is readily confirmed through XRD. Second, the unannealed product does not contain a significant quantity of carbon. EDX analysis failed to detect any carbon in the product powder. Third, the infrared spectrum of the as-prepared powder is free of high-frequency peaks that might be attributed to C–H or N–H stretching modes. These latter two points strongly suggest that the unannealed powder is completely inorganic. Fourth, the Raman spectrum of the as-prepared powder closely matches previously reported spectra and is particularly similar to those obtained from nanocrystalline GaN films prepared by ion-assisted deposition.<sup>14</sup> Fifth, and finally, the product yield was 93% when calculated on the assumption that GaN is the product.

The GaN powder produced in this work shows strong band gap photoluminescence (PL) emission with negligible emission from trap states. Figure 3a shows UV absorption and PL emission spectra (320 nm excitation) from a methanol suspension containing GaN nanopowder that was prepared in pure ether and annealed at 310 °C for 3 h. The emission peak appears at the GaN band gap energy, 3.4 eV. A second peak due to trap state emission is observed at 2.65 eV (468 nm), but this peak is less than one-tenth the intensity of the main bandedge emission peak. Unannealed samples prepared in pure ether gave a strongly blue-shifted PL emission at 4.04 eV (307 nm, Figure 3b) with a peak shape similar to that observed in the annealed sample. This blue-shifted PL peak provides evidence for quantum confinement in these

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**Figure 4.** HRTEM images of GaN nanocrystals annealed at 300 °C for 3 h. Measured lattice spacings correspond to (a) (100) spacing in wurtzite GaN and (b) (200) spacing in zinc blende GaN.

samples and suggests the possibility of adapting this reaction for production of GaN quantum dots. The UV absorption spectrum of the as-prepared suspension (also shown in 3b) shows a blue-shifted absorption edge, also characteristic of electronic quantum confinement.

High-resolution transmission electron microscopy (HR-TEM) images of the sample annealed at 310 °C revealed nanosized crystals of differing phases averaging approximately 10 nm in diameter. Wurtzite and zinc blende crystals were easily identified by measurement of (100) and (200) plane spacings, respectively. Representative images of these two phases are shown in Figure 4, along with the measured lattice spacing. Many crystals were also found with lattice spacings of 0.260 nm, which is consistent with both the (002) spacing of wurtzite GaN and the (111) spacing of zinc blende GaN. No spacings consistent with the rocksalt form of GaN were found in these HRTEM images. Although it is possible for the wurtzite and zinc blende phases to coexist in the same crystal as stacking faults, we did not find any TEM evidence for this in these samples.

Imaging of unannealed samples was attempted with little success. The low contrast produced by nanoparticles of GaN combined with the amorphous nature of the unannealed particles made it difficult to identify the GaN product under the TEM with any confidence.

The mechanism of the reaction and the action of the ether are uncertain. The  $\text{Li}_3\text{N}$  precursor is not well-dissolved by either the ether or the benzene/ether mixture. The ether demonstrably accelerates the reaction, and this acceleration may be due to complexation of the ether with  $\text{GaCl}_3$  to produce a species with enhanced reactivity toward  $\text{Li}_3\text{N}$ . The activating effect of the ether could also be connected to

interactions between the ether and Li ions at the  $\text{Li}_3\text{N}$  particle surface. Interactions between Li and oxygen lone-pair electrons might facilitate Li–N bond cleavage, thus activating the nitride toward attack by  $\text{Ga}^{3+}$ . The poor solubility of  $\text{Li}_3\text{N}$  means that the reaction is likely a surface process. Whether the nascent GaN particle remains at the  $\text{Li}_3\text{N}$  surface after Ga–N bond formation, and for how long, remains an open question. Nevertheless, it seems likely that the  $\text{Li}_3\text{N}$  particle size influences the reaction rate.

Strong electronic quantum confinement in the as-prepared particles was unexpected, because no surface capping ligand was added to restrict particle growth. The most likely explanation for the observed quantum confinement is that the simultaneous formation of LiCl and GaN bonds in proximity at the surface results in the formation of nano-domains of GaN that are entirely surrounded by LiCl, thus giving rise to the quantum-confined PL emission in the as-prepared product. Absent any capping ligand in the mixture, the most likely protective cap on the GaN particles is LiCl. HRTEM images of samples that were annealed at 300 °C without removing LiCl showed numerous examples of adjacent GaN and LiCl domains.

Although this metathesis reaction has been previously studied by others, the activating effect of diethyl ether reported here represents a significant advance in the production of GaN powders. The ether bath regulates the reaction temperature so that product decomposition is avoided, yet unlike other solvents and additives, the ether does not completely quench the reaction or compromise yield. This method appears to be the most practical yet reported for synthesis of nanocrystalline GaN. It should permit easy scale up and may eventually be adapted for production of colloidal GaN quantum dots.

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**Supporting Information Available:** Experimental details of the synthesis and characterization of the GaN nanopowders (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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