

# Gallium Nitride Synthesis Using Lithium Metal as a Nitrogen Fixant

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Micron-sized particles of gallium nitride were synthesized at temperatures as low as 300 °C under ammonia in anhydrous conditions. Two different syntheses were investigated: compound **1** was synthesized using a physical mixture of gallium and lithium under flowing ammonia; compound **2** was synthesized using a gallium/lithium alloy under flowing ammonia. These two methods relied on the presence of lithium metal acting as a nitrogen-fixing and transport agent for metallic gallium. Powder X-ray diffraction demonstrated the purity and crystalline nature of the resulting white gallium nitride; it was found to exhibit extraordinary crystallinity considering its formation conditions. Elemental analysis also determined the purity of **1** and **2** and showed an absence of the lithium impurity in the former, as contrasted with 0.23% Li in the latter. SEM demonstrated the particle sizes of **1** and **2** to be on the micron scale.

## Introduction

Gallium nitride is an important semiconductor due to its impressive properties.<sup>1</sup> Processes such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) are under intense scrutiny as methods of producing thin monocrystalline layers of gallium nitride.<sup>2</sup> However, one impediment to the production of these layers is the lack of a suitable substrate for growth. One possible solution to this problem is the use of single-crystal gallium nitride as a substrate. Recent examples of GaN crystal growth employ a variety of synthetic paths for crystal formation.

Porowski and co-workers have investigated high-pressure (up to 20 kbar) synthesis at elevated temperature (1800 K).<sup>3</sup> Crystals on the millimeter scale are grown by this method using gallium and nitrogen as starting materials. Millimeter-sized crystals are also seen from gallium under a nitrogen pressure generated from the decomposition of NaN<sub>3</sub>.<sup>4</sup> The conjecture of this investigation is that sodium forms an alloy with gallium and mediates the nucleation of GaN on the alloy surface. Also from gallium metal, 0.5 mm crystals were formed upon reacting gallium metal with a flow of NH<sub>3</sub>/N<sub>2</sub> between 1000 and 1150 °C.<sup>5</sup> An older work showed crystal growth from GaN powder, under a flow of

ammonia at 1150 °C.<sup>6</sup> Crystals of up to 5 mm in length were formed.

Two other works employ the interesting idea of using lithium as a nitrogen fixant. The first of these reported gallium nitride crystal formation using Li/Ga alloy and flowing ammonia.<sup>7</sup> The authors used a 1:1 alloy of the metals and found that crystals of up to 5 mm formed between 400 and 500 °C, although these were heavily doped with lithium. The second investigation using lithium was the “ammonothermal” method.<sup>8</sup> Therein, lithium amide was used as a “mineralizer” in an ammonia environment and was found to influence crystal growth and morphology. Unfortunately, this publication made no reference to particle size.

One important aspect in the synthesis of gallium nitride is the purity of the final product. With the increased study of this material, inexpensive routes to pure powder for crystallization reactions are necessary. Precursor-based methods for producing III–V materials are reviewed by Wells and Gladfelter,<sup>9</sup> while several syntheses of microcrystalline or powder GaN from the elements have also been reported.<sup>10–13</sup> The colors of these reported materials range from off-white<sup>11</sup> to black.<sup>12,13</sup> Pure gallium nitride is expected to be a clear crystalline material due to its large band gap. The first

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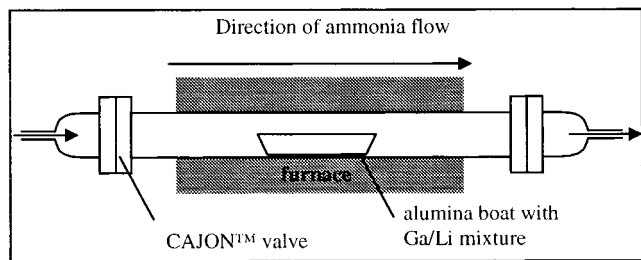
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**Figure 1.** The flow reactor used in the experiment. Arrows at the ends indicate the flow direction from the ammonia tank, over the Ga/Li mixture and out through a mercury bubbler.

reported synthesis of GaN was the reaction of gallium and flowing ammonia at 700 °C, although a temperature of 1000 °C was needed in order to produce an appreciable amount of powder.<sup>14</sup> To produce GaN quantitatively, this reaction required an initial evacuation at 650–680 °C to rid the gallium of incidental oxide.<sup>15</sup>

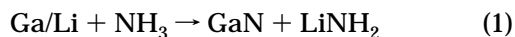
This present work centers on the synthesis of white, microcrystalline gallium nitride from gallium and ammonia, using lithium to increase the solubility of nitrogen-containing species in the metal phase. Although Grimmeiss and co-workers first reported this reaction in 1960,<sup>7</sup> we sought to clarify this work by quantifying the inclusion of the lithium impurity, which was reported, and to circumvent this problem.

First, a physical mixture was subjected to flowing ammonia, and the resulting gallium nitride was characterized with emphasis on the elemental content and crystallinity of the product. A Ga/Li alloy was also subjected to these conditions. This material was also characterized with special attention to its purity and crystallinity.

## Results

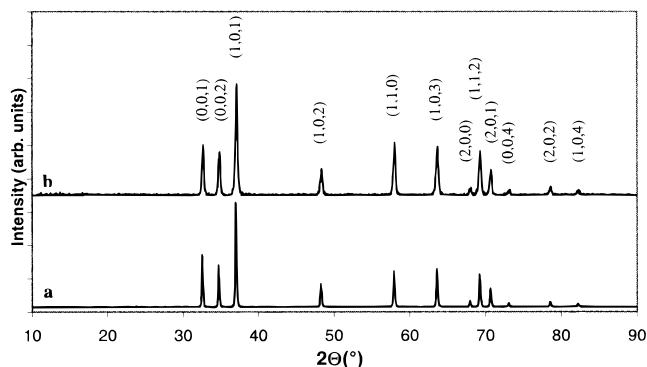
The flow reactor was charged with a physical mixture of 1:1 gallium and lithium (Figure 1). Upon room-temperature introduction of ammonia to the reaction vessel, a brassy-orange metallic solution was formed, which was taken as indication that the lithium was solvating itself with NH<sub>3</sub>.<sup>16</sup>

Under flow, the mixture was heated to 1000 °C over 2 h, held there for 1 h, and then cooled for 2 h. It is likely to have followed the reaction proposed by Grimmeiss:<sup>7</sup>



After the reaction was completed, the synthesized mixture of gallium nitride and lithium nitride was surprisingly white. Since there was a very small amount of a liquid metal impurity, the contents of the reactor were washed with water and then aqua regia. The compacted powder reacted with the water, and a qualitative (flame) test found lithium cation in the wash water.

After the acid was decanted and the product was rinsed repeatedly with water and then acetone, the

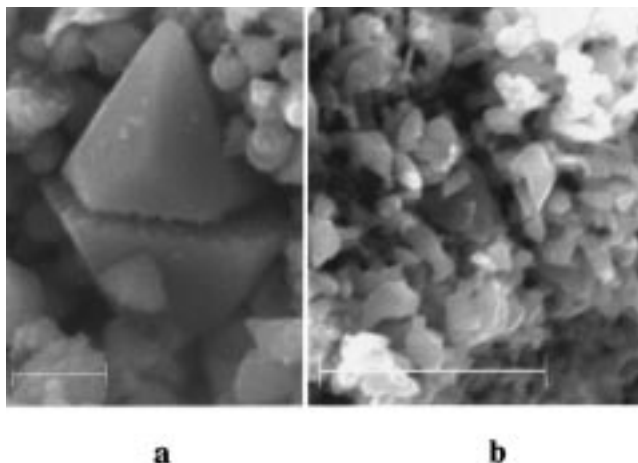


**Figure 2.** The powder X-ray diffractograms of (a) **1** and (b) **2**. Each peak is annotated with its Miller index.<sup>17</sup>

**Table 1. Elemental Analyses<sup>a</sup> for Compounds **1** and **2****

	wt %		
	gallium	nitrogen	lithium
<b>1</b>	83.4	16.7	<0.005 <sup>b</sup>
<b>2</b>	83.0	15.9	0.23
calcd	83.3	16.7	0

<sup>a</sup> The gallium and lithium results were determined by inductively coupled plasma (ICP) measurements, while the nitrogen results were determined by combustion analysis. <sup>b</sup> The detection limit of the ICP.



**Figure 3.** (a) A scanning electron micrograph of **1**. The bar at the bottom of the photo indicates 1 μm. (b) A scanning electron micrograph of **2**. The bar at the bottom of the photo indicates 3 μm.

resulting white powder was found to exhibit the powder X-ray diffractogram (PXRD) (Figure 2a) of crystalline gallium nitride (**1**). Elemental analysis by a combination of inductively coupled plasma (for gallium, lithium, and trace metals) and combustion analysis (for nitrogen) (Table 1) found the material to be very pure, with less than the detectable limit of lithium. SEM demonstrated that the particle size was on the micron scale (Figure 3a).

Since the absence of lithium in **1** refuted a previous literature report,<sup>7</sup> an alloy of lithium and gallium (1:0.1 Ga:Li) was submitted to the same experimental conditions. Unlike the physical mixture, there was no evidence of ammonia solvation at room temperature. Upon completion of the reaction, the material was extremely compacted and gray in color. It was washed with water and again lithium cation was found in the wash. It was cleaned with aqua regia and then rinsed

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with water and acetone. The resulting gray powder (**2**) was shown to be gallium nitride by PXRD (Figure 2b), and elemental analysis found 0.23% (by weight) lithium as an impurity, which represented approximately one-quarter of the lithium used in the reaction. The particle size of **2** was comparable to that of **1** (Figure 3b).

### Discussion

The powder X-ray diffractograms for both materials exhibited excellent crystallinity (Figure 2).<sup>17</sup> Subsequent reactions similar to the synthesis of **1** have demonstrated formation of gallium nitride under flowing ammonia at temperatures as low as 300 °C, but with considerably poorer yields. Although there was only a trace of gallium nitride produced over 1 h at this temperature, it again showed excellent crystallinity.

When the experiment was performed at 500 °C, the yield of lithium-free GaN was 45% in 24 h. In direct contrast to this, no detectable gallium nitride was formed when only gallium was subjected to flowing ammonia at 500 °C for 24 h. This clearly demonstrates the utility of lithium for fixing ammonia for reaction with gallium. From eq 1, we expect lithium amide to form during the reaction, and lithium amide melts at 380 °C. It is possible that nitrogen is made available at the phase boundary of molten lithium amide and gallium metal, as the absence of lithium in the final product suggests a lack of miscibility of the two phases.

There is obviously a crystallization mechanism upon—or after—formation of the material, and there were no crystalline impurities by PXRD. The low-temperature crystallization of these materials indicates that lithium not only plays a role in the synthesis of gallium nitride but in its crystallization as well. It is possible that the lithium amide/gallium interface allows crystallites to form up to a certain size, where they become too heavy and drop away, exposing the surface for more nucleation events. A much weaker spectrum with broader, less defined peaks is expected from a material in which crystallization was not efficient.<sup>18</sup>

The SEM micrographs demonstrated clearly that the particles formed are on the submicron scale for both compounds (Figure 3). The shapes of both **1** and **2** show definite crystallinity, since well-defined edges and flat facets were obvious. This suggests that there is crystallization occurring, but the rate of nucleation exceeds the crystal growth, and thus a very fine microcrystalline powder is produced. Optimizing the conditions of this reaction to promote larger crystal growth is an area of ongoing study in our group.

It is interesting to note that there was no discernible difference between **1** and **2**, with the exception of lithium contamination in the case of **2**. Particle size and crystallinity were the same in both cases. Since the lithium in the physical mixture was very obviously solvated, and indeed formed a liquid solution with ammonia (see experimental), it is possible that this solvation during the synthesis of **1** prevented intercalation of lithium, leading to its improved purity. There was no obvious solvation in the case of **2**; the surface

maintained a highly reflective appearance during the room-temperature addition of NH<sub>3</sub>.

It should also be noted that samples of **1** synthesized in an alumina boat were found to contain aluminum levels of 0.48%, but when a glassy carbon boat was employed, these levels dropped below the detection limit.

### Conclusion

An easy and economical laboratory technique for the synthesis of pure gallium nitride resulted in the formation of **1** from a physical mixture of lithium and gallium. Compound **1** had excellent purity and crystallinity and was produced in a high yield. When the alloy of gallium and lithium was employed in the flow reactor, the yield and purity suffered, but the crystallinity and particle size of **2** were similar to those of **1**. Since the goal of this research is to produce pure GaN powder for subsequent use in recrystallization experiments, purity is of the utmost importance, and the first method holds much promise.

### Experimental Section

**General Considerations.** The reactor was assembled in a Vacuum Atmospheres Company MO-10-M drybox under an inert argon atmosphere. 99.9% lithium and 99.9999% gallium were used as received from Aldrich. Anhydrous ammonia was used as received from Matheson. Powder X-ray diffraction (PXRD) spectra were collected as continuous scans on a Scintag PAD X  $\Theta$ - $\Theta$  diffractometer using a Cu K $\alpha$  X-ray source and a solid-state intrinsic germanium detector. Microscopy was performed on a Leica Stereoscan 440 scanning electron microscope. Leco (St. Joseph, MI) performed the combustion analyses, and Crystal System Compounds (Freeville, NY) performed the ICP analyses.

**Synthesis of Gallium Nitride from a Physical Mixture of Li and Ga, under Flowing NH<sub>3</sub> (1).** A 1:1 molar ratio of gallium (1.12 g, 0.016 mol) and lithium (0.11 g, 0.016 mol) was mixed in a vial and transferred to an alumina reaction boat. This boat was inserted in the flow reactor and the reactor was sealed. The reactor was then placed in a tube furnace and attached to an ammonia cylinder. The system was purged with ammonia for 15 min and then the furnace was ramped to 750 °C over 2 h. After ramping, the furnace was held at 750 °C for 1 h and then allowed to cool to room temperature over 2 h. A solid mass of white material with some metallic liquid resulted, and this material was washed with distilled water and then soaked in aqua regia for 16 h. The resulting powder, after being washed with water and then acetone, was found by PXRD to be gallium nitride (**1**) (1.10 g, 0.013 mol, 82.8% yield).

PXRD ( $d$  (Å), relative intensity): (2.74, 48), (2.58, 39), (2.43, 100), (1.88, 22), (1.59, 35), (1.46, 36), (1.38, 5), (1.36, 32), (1.33, 18), (1.29, 3), (1.21, 4), (1.17, 2). Lit.<sup>17</sup> XRD ( $d$  (Å), relative intensity, ( $h,k,l$ )): (2.76, 70, (1,0,0)), (2.59, 50, (0,0,2)), (2.43, 100, (1,0,1)), (1.88, 60, (1,0,2)), (1.59, 90, (1,1,0)), (1.46, 80, (1,0,3)), (1.38, 20, (2,0,0)), (1.36, 80, (1,1,2)), (1.33, 70, (2,0,1)), (1.30, 20, (0,0,4)), (1.22, 50, (2,0,2)), (1.17, 40, (1,0,4)). Elemental Anal. Calcd: Ga, 83.3; N, 16.7. Found: Ga, 83.4; N, 16.7.

**Synthesis of Gallium Nitride from an Alloy of Li and Ga, under Flowing NH<sub>3</sub> (2).** A 1:0.1 molar ratio of gallium (4.52 g, 0.065 mol) and lithium (0.045 g, 0.0065 mol) was melted together in a vial and transferred to a graphite reaction boat. This boat was inserted in the flow reactor and the reactor was sealed. The reactor was then placed in a tube furnace and attached to an ammonia cylinder. The system was purged with ammonia for 15 min and then the furnace was ramped to 600 °C over 1 h. After ramping, the furnace

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was held at 600 °C for 3 h and then allowed to cool to room temperature over 2 h. A solid mass of gray material with some metallic liquid resulted and this material was washed with distilled water and then soaked in aqua regia for 12 h. The resulting powder, after being washed with water and then acetone, was found by PXRD to be gallium nitride (**2**) (0.88 g, 0.011 mol, 16% yield).

PXRD: ( $d$  (Å), relative intensity): (2.74, 42), (2.57, 39), (2.42, 100), (1.88, 23), (1.59, 45), (1.46, 43), (1.38, 43), (1.35, 39), (1.33, 21), (1.29, 4), (1.22, 6), (1.17, 4). Lit.<sup>17</sup> XRD ( $d$  (Å), relative intensity, ( $h,k,l$ )): (2.76, 70, (1,0,0)), (2.59, 50, (0,0,2)), (2.43,

100, (1,0,1)), (1.88, 60, (1,0,2)), (1.59, 90, (1,1,0)), (1.46, 80, (1,0,3)), (1.38, 20, (2,0,0)), (1.36, 80, (1,1,2)), (1.33, 70, (2,0,1)), (1.30, 20, (0,0,4)), (1.22, 50, (2,0,2)), (1.17, 40, (1,0,4)). Elemental Anal. Calcd: Ga, 83.3; N, 16.7. Found: Ga, 83.0; N, 15.9; Li, 0.23.

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