Rapid Synthesis of Crystalline Gallium Nitride from Solid Precursors at Atmospheric Pressure

Charles H. Wallace, Thomas K. Reynolds, and Richard B. Kaner*

Department of Chemistry and Biochemistry and Exotic Materials Institute, University of California, Los Angeles, Los Angeles, California 90095-1569

Received March 24, 1999
Revised Manuscript Received July 16, 1999

The future of full-colored, flat panel displays, blue lasers, and optical communication is likely to be based on GaN, a wide band gap III−V semiconductor.[1] Here we present an efficient process for rapidly producing crystalline gallium nitride. This method combines the solid precursors gallium(III) iodide, lithium nitride, and ammonium chloride to form highly crystalline GaN without external heating or nitrogen pressure. All the energy needed to synthesize and crystallize gallium nitride is derived from the enthalpy of formation of stable byproduct salts. The GaN produced by this reaction is phase pure by powder X-ray diffraction and luminesces strongly in the blue/UV region.

Polycrystalline GaN is usually made by heating gallium oxides, gallium halides, or gallium metal at elevated temperatures (>750 K) in an ammonia atmosphere for extended periods of time.[2] Other synthetic methods including plasma assisted nitridation, microwave heating, and the use of polymeric or single-source precursors has been developed recently.[3] The resulting materials often contain impurities, are poorly crystalline, and/or display weak photoluminescence. Unfortunately, once formed, GaN cannot be readily annealed without applying pressure since it decomposes at 1150 K under ambient conditions.[4] Single crystals can be grown under high pressure (>2 GPa for ≈20 h)/high temperature (1700−1800 K) conditions or by the use of sodium fluxes.[4,5]

Recently we have demonstrated that gallium nitride can be synthesized directly using a solid-state metathesis (exchange) reaction between gallium(III) iodide and lithium nitride at 4.5 GPa of pressure.[6] The reaction reaches a maximum adiabatic temperature (T_{ad}) of 1443 K in less than a second, which allows the instantaneous formation and crystallization of gallium nitride. Adiabatic reaction temperatures are calculated using temperature-dependent heat capacities with the assumptions of complete reaction and no heat lost to the surroundings.[7] Without the addition of pressure during the gallium(III) iodide/lithium nitride reaction, gallium metal and nitrogen gas are produced.[8] The reason for this is evident from the phase diagram of the Ga/N system.[9] At temperatures >1200 K, it is necessary to apply >1.0 GPa of nitrogen overpressure in order to make GaN the thermodynamically favorable product.[9] Two options are then presented to synthesize GaN directly through solid-state metathesis reactions. The first option is to raise the pressure to a region where GaN is the thermodynamically favorable phase; this has been successful at 4.5 GPa, as we recently reported.[6] The second option is to lower the reaction temperature sufficiently so that pressure will not be needed; this possibility is explored here.

The addition of inert additives (e.g., salt) to metathesis reactions has been used to lower reaction temperatures, often leading to less crystalline products.[10] For the gallium(III) iodide/lithium nitride reaction, salt additives are of interest since significantly lower reaction temperatures could potentially produce gallium nitride at atmospheric pressure. Initial experiments were carried out in which the inert salts NaCl, LiCl, LiI, and their low melting eutectics were added to solid-state metathesis reactions between gallium(III) iodide and lithium nitride. The presence of these inert salts lowers the average reaction temperature by acting as a heat sink and diluting the reactants; however, no crystalline GaN was produced. From the results of these experiments, it appears necessary to use a reactive salt which not only lowers the reaction temperature but also participates in the reaction.

One way to lower the reaction temperature is to change the precursors involved in the reaction given in eq 1. By changing the gallium halide salt (GaX_3) from

$$GaX_3 + Li_3N \Rightarrow GaN + 3LiX \qquad (1)$$

the iodide GaI_3 ($\Delta H_{RXN} = -515$ kJ/mol, $T_{ad} = 1443$ K) to the bromide, $GaBr_3$ ($\Delta H_{RXN} = -611$ kJ/mol, $T_{ad} = 1593$ K), to the chloride, $GaCl_3$ ($\Delta H_{RXN} = -645$ kJ/mol, $T_{ad} = 1656$ K), to the fluoride, GaF_3 ($\Delta H_{RXN} = -627$ kJ/mol, $T_{ad} = 1954$ K), the maximum adiabatic reaction

---

* To whom requests for information should be addressed: Richard B. Kaner kaner@chem.ucla.edu.

(1) (a) Nakamura, S. *Nature* **1998**, *281*, 956. (b) Ponce, F. A.; Bour, D. P. *Nature* **1997**, *386*, 351.

(2) (a) Addamiano, A. *J. Electrochem Soc.* **1961**, *108*, 1072. (b) Elwell, D.; Feigelson, R. S. *J. Cryst. Growth* **1984**, *66*, 45. (c) Balkas, C. M.; Davis, R. F. *J. Am. Ceram. Soc.* **79**, **1996**, *9*, 2309. (d) Dwilinski, R.; Wysmolk, A.; Baranowski, J.; Kaminska, M.; Doradzinski, R.; Gorczynski, J.; Sierzputowski, L.; Jacobs, H. *Acta Phys. Pol., A* **1995**, *88*, 5. (e) Argoitia, A.; Hayman, C. C.; Angus, J. C.; Wang, L.; Dyck, J. S.; Kash, K. *Appl. Phys. Lett.* **1997**, *70*, 179. (e) Balkas, C. M.; Davis, R. F. *J. Am. Ceram. Soc.* **1996**, *79*, 2309.

(3) (a) Hwang, J.-W.; Campbell, J. P.; Kozubowski, J.; Hanson, S. A.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* **1995**, *7*, 517. (b) Neumayer, D. A.; Ekerd, J. G. *Chem. Mater.* **1996**, *8*, 9. (c) Gonsalves, K. E.; Carlson, G.; Rangarjan, S. P.; Benaissa, M.; Jose-Yacaman, M. *J. Mater. Chem.* **1996**, *6*, 1451. (d) Janik, J. F.; Wells, R. L. *Chem. Mater.* **1996**, *8*, 2708. (e) Houmes, J. D.; zur Loye, H.-C. *Chem. Mater.* **1996**, *8*, 2551.

(4) (a) Karpinski, J.; Jun, J.; Porowski, S. *J. Cryst. Growth* **1984**, *66*, 1. (b) Grzegory, I.; Jun, J.; Bockowski, M.; Krukowski, S. T.; Wroblewski, M.; Lucznik, B.; Porowski, S. *J. Phys. Chem. Solids* **1995**, *56*, 639. (c) Porowski, S. *Acta Phys. Pol., A* **1995**, *87*, 295. (d) Pisch, A.; Schmid-Fetzer, R. *J. Cryst. Growth* **1998**, *187*, 329.

(5) Yamane, H.; Shimada, M.; Clarke, S. J.; DiSalvo, F. J. *Chem. Mater.* **1997**, *9*, 413.

(6) (a) Wallace, C. H.; Rao, L.; Rose, G.; Kim, S.-H.; Heath, J. R.; Nicol, M.; Kaner, R. B. *Appl. Phys. Lett.* **1998**, *72*, 596. (b) Wallace, C. H.; O'Loughlin, J. L.; Rao, L.; Kim, S.-H.; Heath, J. R.; Nicol, M.; Kaner, R. B. *Rev. High-Pressure Sci. Technol.* **1998**, *7*, 1040.

(7) Rao, L.; Gillan, E. G.; Kaner, R. B. *J. Mater. Res.* **1995**, *10*, 353.

(8) (a) Fitzmaurice, J. C.; Hector, A.; Rowley, A. T.; Parkin, I. P. *Polyhedron* **1994**, *13*, 235. (b) Parkin, I. P. *Chem. Soc. Rev.* **1996**, *25*, 199.

(9) Karpinski, J.; Jun, J.; Porowski, S. *J. Cryst. Growth* **1984**, *66*, 1.

(10) (a) Wiley, J. B.; Kaner, R. B. *Science* **1992**, *255*, 1093. (b) Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996**, *8*, 333.

10.1021/cm9901764 CCC: $18.00

Table 1. Summary of Molar Ratios of Reactants Used in the Attempted Synthesis of GaN at Ambient Pressure

molar ratios			
GaI_3	Li_3N	NH_4Cl	product(s)
1	1	0.5	Ga + N_2
1	1	1	Ga + N_2
1	1	1.5	Ga + N_2
1	1.33	0.5	Ga + N_2
1	1.33	1	crystalline GaN
1	1.33	1.5	poorly crystalline GaN
1	1.33	2	poorly crystalline GaN
1	1.33	2.5	Ga + N_2
1	2	0.5	Ga + N_2
1	2	1.5	Ga + N_2
1	2	2	poorly crystalline GaN
1	2	2.5	poorly crystalline GaN
1	2	3	highly crystalline GaN
1	2	3.5	Ga + N_2
1	2	4	Ga + N_2
1	2	6	Ga + N_2

temperature increases from 1443 to 1954 K. Unfortunately, this higher reaction temperature simply favors the formation of gallium metal and nitrogen gas (rather than GaN) as is observed experimentally. A second option is to change the nitrogen source. The nitriding agents Mg_3N_2 and Ca_3N_2, which have been used successfully in other metathesis reactions,[11] were substituted for Li_3N; however, these reactions did not propagate. Propagation occurred in reactions where NaN_3 was substituted for Li_3N or when a mixture of both precursors was used. Sodium azide has proven to be a useful nitriding agent in the synthesis of other nitrides since it adds a nitrogen overpressure to metathesis reactions.[8,10,12] Many combinations of lithium nitride and sodium azide were attempted in order to increase the local nitrogen pressure in hopes of synthesizing GaN at atmospheric pressure; however, all simply produced gallium metal and nitrogen gas. This may be attributed to NaN_3 raising the adiabatic reaction temperature and again favoring the formation of gallium and nitrogen rather than GaN.

After unsuccessful attempts with inert salt additives and other nitriding agents, we began investigating the use of ammonium chloride (NH_4Cl) as a reactive salt additive for the formation of gallium nitride. The addition of ammonium chloride to the gallium(III) iodide/lithium nitride reaction (eq 2) in the proper ratio can yield crystalline gallium nitride under *ambient* pressure conditions.

$$GaI_3 + Li_3N + NH_4Cl \Rightarrow GaN + 3LiI + NH_3 + HCl \quad (2)$$

The solid precursors, gallium(III) iodide, lithium nitride, and ammonium chloride were weighed out in the molar ratios given in Table 1 in an inert helium atmosphere. The reactants were then ground together in an agate mortar and placed in a steel reactor modeled after a bomb calorimeter.[13] The steel reactor was equipped with a Nichrome wire that was resistively heated to initiate the reaction. After ignition, the reactions propagated rapidly (<1 s), reaching maximum adiabatic temperatures of 613−1443 K, depending on the amount of ammonium chloride added. The products cooled to near room temperature in less than a minute. The products were then removed from the inert atmosphere and washed to remove the salt byproducts. Generally it was found to be useful to wash the reaction products in a dilute acid (0.5 M HCl(aq)) solution in order to remove any unreacted starting materials that could react with water during the washing process to form gallium oxides or hydroxides (i.e., GaO_2H and/or $Ga(OH)_3$) and contaminate the product. Gallium nitride is not affected by the acid wash since it has been determined that GaN is extremely resistant to attack by HCl.[14] After being rinsed in water, the gallium nitride product was then isolated using vacuum filtration and dried in air.

Ammonium chloride (NH_4Cl), in contrast to the inert salt additives LiCl, LiI, or NaCl does participate in the GaN reaction as a reactive nitrogen source. The nitriding ability of ammonium chloride is demonstrated in a metathesis reaction between $TaCl_5$, CBr_4, Mg, and NH_4Cl in which tantalum carbide was the expected product; however, cubic tantalum nitride (TaN) was found to be the only crystalline product after washing. In addition, a related salt, ammonium fluoride, is known to aid in the nitridation of silicon to silicon nitride in a self-propagating high-temperature synthesis.[15]

The solid-state metathesis reaction between GaI_3 and Li_3N (eq 1) is highly exothermic and expected to reach a maximum adiabatic temperature of 1443 K, the boiling point of the byproduct salt, LiI. The addition of ammonium chloride serves two purposes. First, it can potentially lower the adiabatic temperature down to 613 K, the sublimation point of NH_4Cl. For example, calculated values of T_{ad} decrease from 1264 to 742 K as the amount of NH_4Cl added to the GaI_3+Li_3N reaction is increased from 1 to 2 mol. Second, ammonium chloride serves as a reactive nitrogen source. Ammonium chloride does this by decomposing into an equimolar mixture of NH_3 and HCl.[16] This leads to a tradeoff between the reaction temperature and the ammonia pressure produced by the decomposition of NH_4Cl. Hence, the gallium nitride metathesis reaction is particularly sensitive to the amount of NH_4Cl that is added. It is evident from the data in Table 1 that if too little NH_4Cl is added, the reaction reaches too high of a temperature and preferentially forms Ga metal and nitrogen gas as products. If too much NH_4Cl is added, the reaction does not produce enough heat and/or the reactants are too diluted to form crystalline GaN. Instead, some amorphous GaN forms, which may oxidize to GaO_2H during the washing process.

As a control experiment, NH_4Cl and GaI_3 were heated under vacuum in a sealed quartz tube to 1073 K, however no product formed. No solid remained after

---

(11) Ali, S.; Aguas, M. D.; Hector, A. L.; Henshaw, G.; Parkin, I. P. *Polyhedron* **1997**, *16*, 3635.

(12) Rao, L.; Kaner, R. B. *Inorg. Chem.* **1994**, *33*, 3210.

(13) Bonneau, P. R.; Wiley, J. B.; Kaner, R. B. *Inorg. Synth.* **1995**, *30*, 33.

(14) Johnson, W. C.; Parsons, J. B.; Crew, M. C. *J. Phys. Chem.* **1932**, *36*, 2651.

(15) (a) Rodriguez, M. A.; Makhonin, N. S.; Escrina, J. A.; Brovinkaya, I. P.; Osendi, M. I.; Barba, M. F.; Iglesias, J. E.; Moya, J. S. *Adv. Mater.* **1997**, *7*, 8. (b) Lee, W.-C.; Chung, S.-L. *J. Mater. Res.* **1997**, *12*, 805.

(16) Kirk, R. E., Othmer, D. F., Grayson, M., Eckroth, D., Eds. *Encyclopedia of Chemical Technology*, 3rd ed.; J. Wiley and Sons: New York, 1978; Vol. 2, p 521.

(17) Leszczynski, M.; Suski, T.; Perlin, P.; Teisseyre, H.; Grzegory, I.; Bockowski, M.; Jun, J.; Porowski, S.; Major, J. *J. Phys. D—Appl. Phys.* **1995**, *28*, A149.

(18) Monemar, B. *Phys. Rev. B* **1974**, *10*, 2.

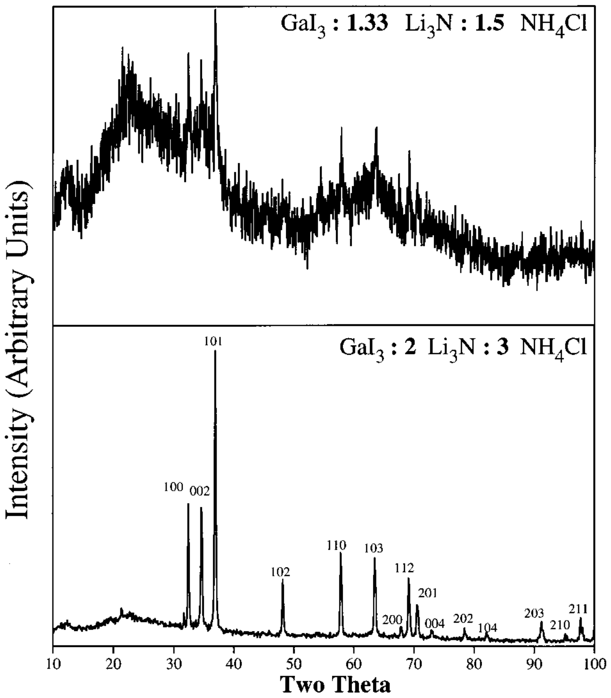

Figure 1. Powder X-ray diffraction patterns of the products of the reaction of GaI_3, Li_3N, and NH_4Cl. A nonideal ratio of reactants such as 1:1.33:1.5 GaI_3:Li_3N:NH_4Cl results in poorly crystalline GaN (upper pattern), while an optimal ratio of 1:2:3 GaI_3:Li_3N:NH_4Cl results in highly crystalline GaN (lower pattern).

washing in water, demonstrating that the addition of Li_3N is necessary to form GaN via a metathesis reaction.

The series of reactions shown in Table 1 needed to be carried out in order to determine the proper molar ratio of the reactants. The reaction that gives the most crystalline GaN for our reaction scale is a 1:2:3 molar ratio of GaI_3:Li_3N:NH_4Cl as shown in Figure 1, bottom. A least squares refinement of the X-ray data indicates that the GaN formed crystallizes in a hexagonal crystal structure with lattice parameters of $a = 3.186(2)$ Å and $c = 5.174(8)$ Å, which is comparable to literature values for hexagonal GaN of $a = 3.1879-3.1894$ Å and $c = 5.1856-5.1865$ Å.[17] The GaN produced in this metathesis reaction is phase pure according to the X-ray diffraction pattern and contains no detectable iodine by energy dispersive spectroscopy. The Ga content of the GaN is 49 mol % (50% expected) as calculated by thermogravimetric analysis carried out in air to 1273 K which converted all of the GaN to Ga_2O_3. This 1:2:3 GaI_3:Li_3N:NH_4Cl reaction has a ΔH of -351.6 kJ and a calculated T_{ad} of 613 K assuming that ammonium chloride acts only as an inert salt. However, assuming that the ammonium chloride is completely reactive as a nitriding agent, the calculated adiabatic temperature is 1128 K. Therefore, it is reasonable to assume that the actual reaction temperature is somewhere between these two extremes.

All experiments reported were carried out on a small (2.5 mmol) laboratory scale, typically 1.075 g GaI_3 + 0.166 g Li_3N + 0.383 g NH_4Cl. Product yield was often only 25% by weight (0.05 g GaN formed, 0.20 g theoretical) for this reaction due to incomplete reactions and losses through handling. If larger amounts of product are desired in a single reaction, then the amount of ammonium chloride added to the reaction likely needs to be increased, since a higher temperature will be maintained for a longer period of time. *Warning*! All metathesis reactions are highly exothermic and great care should be exercised when these reactions are scaled up or if the amounts of reactants are changed.

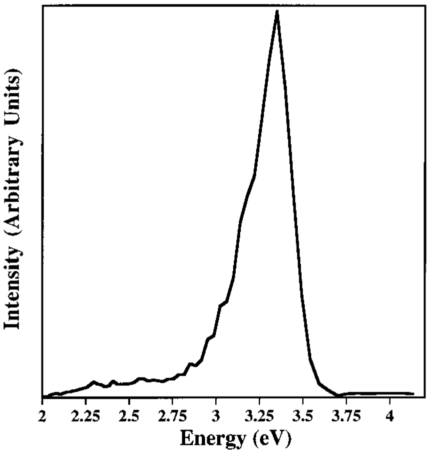

Figure 2. Gated photoluminescence spectrum of gallium nitride produced by the metathesis reactions between GaI_3, Li_3N, and NH_4Cl in a 1:2:3 molar ratio. The room temperature (300 K) spectrum exhibits the band gap of bulk GaN at 3.38(3) eV.

The GaN produced by this process luminesces strongly in the blue/ultraviolet region as can be seen in the room temperature (300 K) photoluminescence spectrum shown in Figure 2. The excitation source is a 5 ns, 20 μJ pulse of 266 nm radiation. The photoluminescence spectrum reveals the 3.38(3) eV band gap characteristic of bulk gallium nitride.[18] Since no additional luminescence is observed at energies higher than the band gap absorption and this absorption is not blue shifted, the photoluminescence measurements are consistent with micrometer-scale, rather than nanometer-scale, crystallites. This is confirmed by scanning electron microscopy measurements which show average particle size around 1 μm and essentially no line broadening in the X-ray diffraction pattern (Figure 1, bottom) when compared to an external silicon standard.

The addition of ammonium chloride to the solid-state metathesis reaction between GaI_3 and Li_3N allows the formation of gallium nitride at ambient pressure. All the energy needed to synthesize highly crystalline gallium nitride is provided by the enthalpy of formation of stable byproduct salts. Ammonium chloride serves as both a heat sink to lower the reaction temperature and as a nitriding agent. The phase pure gallium nitride formed shows intense luminescence in the blue/ultraviolet region. Ammonium chloride will likely prove to be a useful additive in other solid-state metathesis reactions.

Acknowledgment. The authors would like to thank Sang-Ho Kim and Prof. James R. Heath for help with photoluminescence and Dr. Lin Rao for assistance with adiabatic temperature calculations. This work was supported by the National Science Foundation, the UC Campus Laboratory Collaboration program, and the LLNL Materials Research Institute.

CM9901764