Thermal Control of Metathesis Reactions Producing GaN and InN[†]

Robert W. Cumberland, Richard G. Blair, Charles H. Wallace, Thomas K. Reynolds, and Richard B. Kaner*

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

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The addition of lithium amide ($LiNH_2$) and ammonium chloride (NH_4Cl) to metathesis (exchange) reactions between gallium triiodide (GaI_3) and lithium nitride (Li_3N) produces crystalline gallium nitride (GaN) in seconds at ambient pressure. A specially designed rate cell incorporating multiple thermocouples enables both the reaction velocity and temperatures to be measured. Without the additives, the GaI_3/Li_3N reaction propagates at >100 cm/s with a reaction temperature above 1300 K, which exceeds the 1150 K decomposition temperature of GaN. By adding an optimal ratio of $LiNH_2$ and NH_4Cl, the reaction velocity slows to about 3 cm/s with a reaction temperature near 1200 K. Rapid heat dissipation is found to be very important in these reactions in preventing the decomposition of GaN. By using a specially designed thermal dissipation cell, the yield of GaN can be increased up to 78.8%. Applying the concepts developed in the synthesis of GaN, crystalline InN has been synthesized for the first time using solid-state metathesis reactions.

Introduction

Gallium nitride (GaN), indium nitride (InN) and their solid solutions ($Ga_{1-x}In_xN$) are important optoelectronic materials and can be used to fabricate $p-n$ junctions, laser diodes, and full-color, flat-panel displays.[1−3] Light-emitting diodes containing GaN as the active component are significantly brighter than either conventional incandescent light bulbs or gallium phosphide-based devices.[4] Polycrystalline $Ga_{1-x}In_xN$ may prove useful as phosphors for large area displays.

Gallium nitride is typically made by heating gallium, gallium oxide (Ga_2O_3), or gallium halides at elevated temperatures in ammonia for prolonged periods.[5−7] Materials synthesized in this manner are often poorly crystalline, display weak photoluminescence, and/or contain impurities. More recent synthetic methods include single-source and polymeric precursors, plasma-assisted nitridation, and microwave heating.[8−13] Single crystals of gallium nitride can be made at high temperatures (1700−1800 K) given sufficient time and therefore require high pressures (>2 GPa), since GaN decomposes at 1150 K under ambient conditions.[14−18] Alkali metal fluxes have recently proven to be useful for crystal growth.[19−21]

Indium nitride (InN) is an even more difficult material to prepare than GaN since it decomposes at a lower temperature of ≥990 K.[22,23] Commercial indium nitride samples commonly suffer from excess In metal impurities as well as many defects in the form of nitrogen vacancies in the InN lattice. Indium nitride is not a well-studied material and many of its bulk properties are unknown.[24,25] Its main use is in thin film growth to form solid solutions with GaN for light-emitting diodes and potentially for use in tunable laser diodes.[1,26] The thermodynamically stable form of both GaN and InN consists of metal cations in a hexagonal close-packed lattice with nitrogen anions filling half of the tetrahedral sites. Since indium nitride has a direct band gap of 1.9 eV, while gallium nitride has a direct gap of 3.4 eV, solid solutions of the two compounds can tune the band gap to any value throughout the visible spectrum and into the ultraviolet region.

Solid-state metathesis (SSM) reactions have developed over the past decade into an effective method for synthesizing nitrides and other materials that are difficult to make by conventional methods.[27] The driving force behind these rapid reactions is the formation of stable salt byproducts. For example, combining GaI_3 with Li_3N to produce GaN, as given in eq 1, is downhill by −515 kJ/mol.

$$GaI_3 + Li_3N \rightarrow GaN + 3LiI \qquad (1)$$

This is more than four times as energetic as the elemental reaction $Ga + {}^1/_2N_2 \rightarrow GaN$ which is downhill by −110 kJ/mol. The intense heat generated by SSM reactions often generates temperatures of >1300 K in a fraction of a second.

The maximum adiabatic reaction temperature for a SSM reaction can be calculated using temperature-dependent heat capacities assuming that reactions go to completion and no heat is lost to the surroundings.[28] Since the calculated maximum adiabatic temperature of 1443 K for the GaI_3/Li_3N reaction (eq 1) exceeds the GaN decomposition temperature of 1150 K, it is not surprising that this reaction was reported to fail to produce GaN.[29] By applying 4.5 GPa of pressure to the reactants before ignition, we have been able to synthesize highly crystalline GaN in excellent yield (up to 87%) directly from GaI_3 and Li_3N as given in eq 1.[30] Attempts to lower the reaction temperature with inert salt additives such as LiI, LiCl, or NaCl have worked with other SSM reactions, but failed to produce crystalline GaN.[31,32] However, addition of the reactive salt ammonium chloride does enable crystalline GaN to be synthesized without the need for pressure.[32] The tradeoff is a reduced yield of product (∼25%). Because of the inefficiency of this process, new precursors and novel reaction conditions are sought in order to produce higher yields of crystalline GaN. Here we report the use of lithium

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* Corresponding author.

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amide in combination with ammonium chloride to enhance the yield of GaN. This combination of reactive salts also enables InN to be produced for the first time by SSM reactions.

Experimental Section

Chemicals. The purity of the chemical precursors is extremely important because of the sensitivity of these SSM reactions toward water and oxygen. Gallium(III) iodide was prepared from Ga (99.9999% Cerac) and I_2 (99.99% Alfa-Aesar) through a vapor transport reaction in an evacuated sealed Pyrex tube using a temperature gradient from 190 to 300 °C as modified slightly from a literature preparation.[33] The GaI_3 product was further purified by sublimation in an evacuated tube to produce high purity GaI_3. InI_3 was prepared in an analogous manner. Lithium nitride (99.5% Cerac) was used as received and has worked well, whereas lithium nitride purchased from other vendors often contained significant oxygen impurities. Indium(III) bromide (99.9% Alfa-Aesar) and lithium amide (95% Alfa Aesar) were used as received. Ammonium chloride (99.999% Cerac) was dried for 24 h in a vacuum oven at 100 °C. If the ammonium chloride is not completely dry, the crystallinity and yield of the products will be compromised.

XRD Analysis. The products were analyzed with Cu Kα radiation on a Crystal Logic θ-2θ powder X-ray diffractometer. Samples were scanned from 10 to 100° 2θ at 0.1° intervals at 3 s per interval. Analysis and interpretation of the spectra were carried out using the Macintosh software MacDiff.

XRF Analysis. XRF spectroscopy was performed on a Philips Norelco X-ray Fluorimeter with Cr Kα radiation used as an excitation source. The fluorescence X-rays were diffracted with a Pentaerythritol tetrakis(hydroxymethyl)-methane (PET) analyzer crystal. The mass percent of gallium in the product was measured by monitoring Ga Kα radiation and comparing it to a standard curve generated from known masses of GaN (obtained from Cerac).

Photoluminescence. Photoluminescence spectra were obtained from pressed pellets of GaN powder. The excitation source consisted of a Liconix-3220n He−Cd laser with a maximum power of 18 mW. A 325 nm band-pass filter was placed before the sample and a 330 nm cutoff filter was placed after the sample. The spectra were detected with a microchannel plate-PMT(MCP-PMT)-R2809U-05 detector.

Synthesis and Isolation of GaN and InN. All reactions were carried out on a small scale, theoretically producing only 0.25 g of GaN, assuming 100% yield. Most reactions were carried out according to eq 2, where M represents either Ga or In metal and the molar ratios of the additives lithium nitide (x), lithium amide (y), and ammonium chloride (z) were varied.

$$MI_3 + xLi_3N + yLiNH_2 + zNH_4Cl \rightarrow MN + (x - 1)Li_3N + 3LiI \quad (2)$$

Note that eq 2 assumes x is greater than 1 and ignores the possibility that either NH_4Cl and/or $LiNH_2$ can act as a nitrogen source for the production of GaN. The solids GaI_3 or InI_3, Li_3N, NH_4Cl, and $LiNH_2$ were weighed out in the molar ratios given in Table 1 for GaI_3 reactions and in Table 2 for InI_3 reactions. The weighings took place in an inert helium atmosphere so that contamination by oxygen or moisture could be avoided. These reactants were then ground together in an agate mortar and placed in a steel reaction vessel modeled after a bomb calorimeter.[34] The reaction was ignited by resistively heating a piece of Nichrome wire (Omega) and touching it to the reactants. All the reactions propagated quickly and were complete within 1 s. The products cooled to room temperature within 1 min. To remove the byproduct salts, the products were taken out of the inert atmosphere and washed with water or ethanol. To isolate the final powder, the washed products were vacuum filtered or centrifuged and allowed to dry in air.

TABLE 1: A Summary of SSM Reactions between Gallium(III) Iodide, Lithium Nitride, Lithium Amide, and Ammonium Chloride[a,b,c]

reaction no.	GaI_3	Li_3N	$LiNH_2$	NH_4Cl	product(s)
GaN01	1	0	3	0	products dissolved in H_2O
GaN02	2	1	2	1	GaO_2H, Ga_2O_3, $Ga(OH)_3$
GaN03	2	1	2	2	GaO_2H, Ga_2O_3, $Ga(OH)_3$
GaN04	2	1	3	1	GaO_2H, Ga_2O_3, $Ga(OH)_3$
GaN05	6	5	3	3	GaO_2H, Ga_2O_3, $Ga(OH)_3$
GaN06	6	5	4	4	GaO_2H, Ga_2O_3, $Ga(OH)_3$
GaN07	6	6	3	3	35.3% yield GaN
GaN08	6	6	3	4	48.8% (78.8%) yield GaN
GaN09	6	6	4	3	37.4% yield GaN
GaN10	6	6	4	4	39.2% yield GaN
GaN11	10	11	5	5	26.8% yield GaN
GaN12	10	11	6	6	23.4% yield GaN
GaN13	6	7	3	3	8.9% yield **most crystalline GaN**
GaN14	6	7	4	4	15.8% yield GaN
GaN15	3	4	3	3	products dissolved in H_2O
GaN16	1	2	1	1	products dissolved in H_2O
GaN17	1	2	1	2	products dissolved in H_2O
GaN18	1	2	3	2	products dissolved in H_2O
GaN19	1	2	3	3	products dissolved in H_2O

[a] The molar ratios are shown below the reactants and the products of the reaction are shown in the last column; when GaN was produced, the percent yield is shown. [b] All reactions in this table were carried out on a small scale to produce 0.25 g of GaN assuming 100% theoretical yield. [c] The yield of 78.8% for GaN08 was obtained by performing the reaction in the thermal dissipation cell.

TABLE 2: A Summary of SSM Reactions between Indium(III) Iodide, Lithium Nitride, Lithium Amide, and Ammonium Chloride[a,b]

reaction no.	InI_3	Li_3N	$LiNH_2$	NH_4Cl	product(s)
InN01	1	0	1	0	In metal/oxides
InN02	2	0	3	0	In metal
InN03	2	1	2	0	In metal/oxides
InN04	2	1	2	1	In metal/oxides
InN05	4	2	5	2	In metal/oxides
InN06	4	2	5	4	In metal/oxides
InN07	2	1	3	0	InN/In metal
InN08	2	1	3	1	**most crystalline InN**/In metal
InN09	4	2	6	3	In metal/oxides
InN10	2	1	3	2	InN/In metal
InN11	4	2	6	5	In metal/oxides
InN12	4	2	6	6	In metal/oxides
InN13	4	2	6	7	In metal/oxides
InN14	2	1	4	0	In metal/oxides
InN15	2	2	3	3	InN and In metal
InN16	1	1	3	1	In metal/oxides

[a] The molar ratios are shown below the reactants and the products of the reaction are shown in the last column. [b] All reactions in this table were carried out on a small scale to produce 0.25 g InN assuming 100% theoretical yield.

A cell was specially designed for measuring reaction rates and is shown in Figure 1. The cell consists of four machined aluminum silicate ceramic (McMaster-Carr) inner pieces and an upper and lower lid of 308 stainless steel. When assembled, the cell forms a trough 5 cm long, 0.32 cm wide and 0.47 cm tall for an enclosed volume of 0.75 cm^3 and a total surface area of 8.2 cm^2. A length of 28 gauge Nichrome ignition wire (Omega) is placed at one end of the cell and four 0.003 in. K-type thermocouples (Omega) are placed at 1 cm intervals

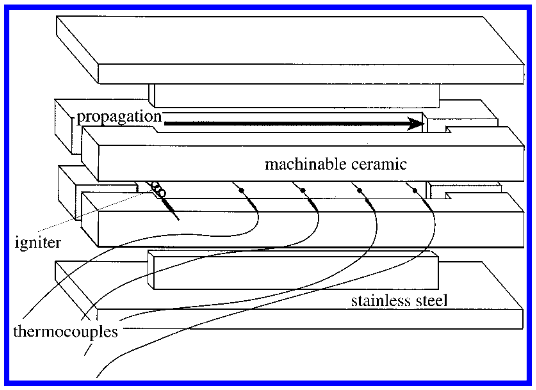

Figure 1. Rate cell for determining reaction propagation rates and T_{max}. The outer two pieces are constructed of 308 stainless steel. The inner pieces are constructed of machineable aluminum silicate.

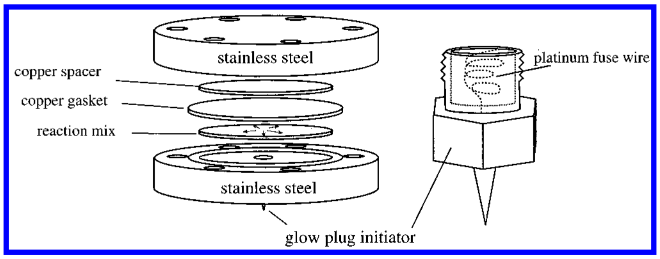

Figure 2. Thermal dissipation cell and close-up of the glow-plug initiator. The glow plug is threaded into the center of the bottom plate of the cell. The small arrows indicate the propagation direction of the metathesis reaction.

from the ignition wire. The reaction mixture is packed around the thermocouples and ignition wire. Each thermocouple consists of 30 cm of K-type thermocouple wire and are connected to a custom-built amplifier and zero-point reference circuit. This circuit was built around four AD595AQ (Analogue Devices) K-type amplifiers and zero-point reference integrated circuits. The device was tuned to amplify the thermocouple signal by a factor of 123. To minimize 60 Hz noise from power supply ripple, the device was powered by lead−acid gel batteries. The output of the device was passed through electrical feed-throughs in the side of a helium-filled glovebox and monitored by a PC using a 6023E (National Instruments) data acquisition board set to take data in differential mode. The initiation of a reaction and collection of data were controlled by a custom LabView (National Instruments) program. The reaction was initiated by applying 3−4 A of DC current at 12 V. A direct current source was used to reduce the AC noise amplified by the thermocouple amplification circuit. A typical data run consisted of applying power to the Nichrome wire for 1400 ms and acquiring data every 0.1 ms for 16−20 s. The data file was then analyzed using Igor Pro (Wavemetrics). Before any analysis was performed, a 55 Hz low-pass filter was applied to further reduce any 60 Hz AC noise.

To maximize the heat transfer effects of the reaction cell, a thermal dissipation cell was designed as shown in Figure 2. The cell consists of two 2.5 in. Del•Seal flanges (MDC) with a solid copper gasket. A 1/4-32 hole was tapped in the center of one flange to allow for the insertion of a glow plug, of the type often used for gas powered model engines (R/C long plug). The glow plug was used as the igniter for reactions in this cell. The reaction mixture was loaded in the void space between the flange with the glow plug and the copper gasket. This space forms a cylindrical reaction area with a height of 0.05 cm and a diameter of 4.14 cm for a total enclosed volume of 0.67 cm^3 and a surface area of 27.57 cm^2.

Results and Discussion

Gallium Nitride. Since GaN decomposes above 1150 K without applied pressure and the SSM reaction between GaI_3 and Li_3N has an adiabatic temperature of 1443 K, finding an additive that could reduce the reaction temperature and create an ammonia atmosphere is a potentially important approach to improving product yield and crystallinity. Lithium amide ($LiNH_2$) was chosen since it is a stable solid at room temperature that decomposes above 720 K to produce gaseous ammonia.[35] Lithium amide has been used effectively in the nitridation of transition metals.[36] Recently, Janik and Wells showed that a polymeric precursor, $\{Ga(NH)_{3/2}\}_n$ (gallium imide), when heated under an inert atmosphere above 725 K decomposes into poorly crystalline gallium nitride.[8] These results suggested that amides might be effective precursors in solid-state metathesis reactions to produce gallium nitride.

The first reactions that were attempted included only gallium(III) iodide, lithium nitride, and lithium amide. The molar ratios of reactants were balanced to produce just salt and ammonia as byproducts as given in eq 3.

$$2GaI_3 + Li_3N + 3LiNH_2 \rightarrow 2GaN + 6LiI + 2NH_3 \quad (3)$$

These reactants readily ignited when touched with a heated Nichrome wire yielding a gray product and copious amounts of gas. To remove the byproduct salts, the products were taken out of the inert atmosphere and washed with water or ethanol. To isolate the final powder, the washed products were vacuum filtered or centrifuged and allowed to dry in air. Percent yields were calculated from the mass of powder isolated versus a theoretical yield assuming all GaI_3 is converted to GaN. Powder X-ray diffraction revealed that the fine gray powder contained gallium nitride as the only crystalline product. This result was very promising even though the product had relatively low crystallinity. When no lithium nitride was used, the reaction still readily propagated after ignition. However, all the products reacted vigorously with water and dissolved during the washing process, indicating that no gallium nitride was produced. By using lithium amide and varying the molar ratios of the reactants as given in Table 1, the product yield, crystallinity, and purity were improved substantially.

As can be seen from Table 1, the reactions with a GaI_3 to Li_3N ratio greater than one to one (i.e., excess GaI_3) produced gallium oxides and hydroxides (e.g., Ga_2O_3 and $Ga(OH)_3$) after washing in water. Conversely, reactions with a GaI_3 to Li_3N ratio significantly less than one to one (i.e., excess Li_3N) produced products that reacted with water and dissolved upon washing. Highly crystalline GaN was only formed when the ratio of GaI_3 to Li_3N was either equal to or slightly less than one-to-one. Table 1 demonstrates how increasing the amount of Li_3N (with respect to GaI_3) tends to increase the crystallinity of the GaN product but simultaneously lowers the yield. Figure 3 clearly shows how the crystallinity of the GaN product steadily increases as the GaI_3-to-Li_3N ratio is changed from 6:6 to 10:11 to 6:7. The most crystalline GaN formed when the molar ratios of GaI_3:Li_3N:$LiNH_2$:NH_4Cl were 6:7:3:3. The X-ray data given in Figure 3 indicate a hexagonal crystal structure with lattice parameters of $a = 3.19$ Å and $c = 5.18$ Å. These values are comparable to the published literature values for hexagonal GaN of $a = 3.1879-3.1894$ Å and $c = 5.1856-5.1865$ Å.[37] The presence of GaN was further confirmed using X-ray fluorescence (XRF) spectroscopy. The product was found to contain ~81% Ga by mass, while pure GaN contains ~83% Ga by mass. The quality of the GaN product was further

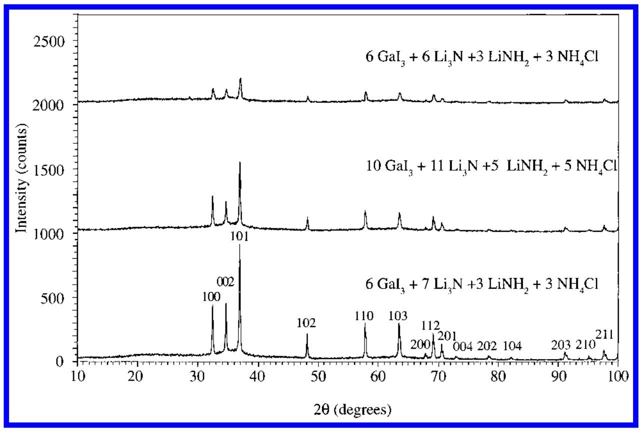

Figure 3. Powder X-ray diffraction patterns which approach the optimal ratios of precursors for the production of gallium nitride. The diffraction patterns are labeled according to the experiments reported in Table 1.

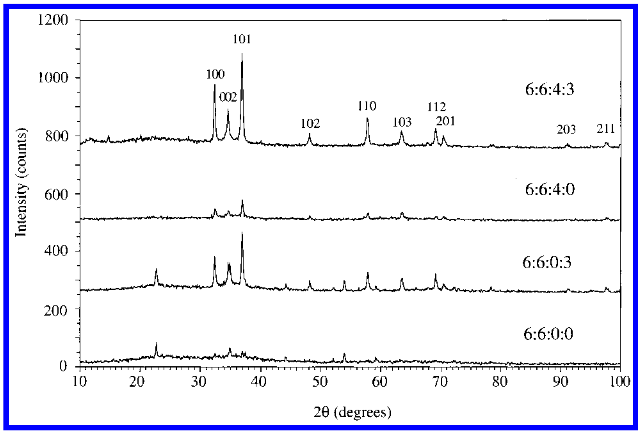

Figure 4. Comparison of GaN-forming reactions. The ratios indicated are GaI_3:Li_3N:$LiNH_2$:NH_4Cl. The Miller indices for GaN are given in the top pattern. The peaks at 22.7 (211), 44.2 (332), 53.8 (440), and 59.2 (611) degrees 2θ in the lower two patterns are for Li_3GaN_2.

investigated by obtaining photoluminescence (PL) spectra directly from the bulk powder. The GaN synthesized from the reaction with a 6:6:4:3 ratio exhibited a strong blue emission at ~3.3 eV with a full width at half maximum of ~0.3 eV. The blue emission is consistent with the known 3.38 eV band gap of bulk GaN.[38]

To elucidate how the addition of $LiNH_2$ and NH_4Cl to GaN-forming reactions can affect the yield and crystallinity of the products, each was systematically removed from the reactants. Four reactions, denoted 6:6:4:3, 6:6:4:0, 6:6:0:3, and 6:6:0:0, represent different combinations of the reactants GaI_3:Li_3N:$LiNH_2$:NH_4Cl. These reactions were carried out in the rate cell (Figure 1) in order to determine propagation velocities and maximum reaction temperatures. Each reaction produced GaN; however, without ammonium chloride the products had relatively low crystallinity as can be seen in Figure 4. The use of dry ethanol as a solvent to isolate the product enabled the identification of a Li_3GaN_2 phase found in the products of the two reactions containing no $LiNH_2$ (Figure 4). This shed light on the role of $LiNH_2$ in these reactions. $LiNH_2$ serves to eliminate the production of the Li_3GaN_2 phase and, therefore, increases the yield of GaN. It can be seen in Table 3 that the maximum temperature measured for a $LiNH_2$-containing reaction (~1290 K) does not differ appreciably from a reaction containing no added salts (~1340 K). In contrast, the addition of NH_4Cl serves to lower the overall reaction temperature by up to 240 K. This can be explained by two phenomena. Since NH_4Cl sublimes at 613 K, the energy needed to supply the heat of sublimation must be taken from the energy generated by the reaction. This serves to lower the overall reaction temperature and to retard the rate of propagation of the reaction. The addition of NH_4Cl and $LiNH_2$ also serve to dilute the reaction mixture. This slows down the reaction rate and lowers the maximum reaction temperature. However, the sublimation of NH_4Cl appears to be the dominant effect.

TABLE 3: Comparison of T_{max}, Propagation Rates, and Products for Various GaN-Forming Reactions[a]

ratio	T_{max} (K)	propagation rate (cm/s)	product(s)
6:6:4:3	1206 ± 38	2.77	GaN
6:6:4:0	1288 ± 43	82.6	GaN
6:6:0:3	1095 ± 72	3.67	Li_3GaN_2, GaN
6:6:0:0	1337 ± 106	>100	Li_3GaN_2, GaN

[a] The ratio indicates the relative amounts of GaI_3, Li_3N, $LiNH_2$, and NH_4Cl, respectively.

Finding that GaN was produced in the reactions without either $LiNH_2$ or NH_4Cl as additives (6:6:0:0 in Figure 4) was unexpected. GaN had not previously been prepared from just GaI_3 and Li_3N at ambient pressure.[29] A logical hypothesis is that heat dissipation is a key factor in producing GaN from such reactions. The standard reaction cell, based on a bomb calorimeter design, consists of a reaction cup open at the top with dimensions of 2 cm in diameter by 1 cm tall. This gives a cell with a maximum internal cell surface area of 9.42 cm^2. In practice, this cup is only filled halfway, further reducing the internal cell surface area to 4−5 cm^2. The cross-sectional area of a reaction is 1 cm^2 at its maximum. Heat must diffuse through a large area of product/reaction mixture to ultimately bleed into the reaction cup. Additionally, GaI_3 sublimes at 618 K and the heat of reaction can drive off GaI_3 resulting in a lower yield and formation of Li_3GaN_2 as a byproduct. The open cup design allows the escape of GaI_3 into the larger cell volume. In contrast, the rate cell has an internal cell surface area of 8.2 cm^2 with a minimal amount of free space for GaI_3 to escape. The cross-sectional area of the reaction mixture is 0.15 cm^2. This allows heat to flow rapidly to the reaction cell walls. However, the reaction cell is not optimal for heat dissipation since it is not isotropic and the ceramic sides of the vessel have a lower thermal conductivity than the stainless steel top and bottom.

To maximize the heat flow in these reactions, a thermal dissipation cell was designed (Figure 2). The desire was to maximize thermal contact with a large heat sink (stainless steel flanges) and minimize the reaction cross section. Additionally, the cell was designed to be a sealed unit to prevent the loss of GaI_3 via sublimation. The final cell design possesses an internal cell surface area of 27.6 cm^2 and a reaction cross section that varies from 0.016 cm^2 to 0.67 cm^2, since the reaction propagates in a ring from the center of the reaction cell. The product obtained from this reaction cell was less crystalline than the product from the standard cell because the mixture does not remain at a temperature favorable for crystallite growth for a long enough period of time. However, reaction yields of up to 78.8% GaN have been obtained. This represents a significant improvement in yield when compared to reactions performed in a conventional cell (see Table 1).

Indium Nitride. By applying the lessons learned from the synthesis of gallium nitride, solid-state metathesis reactions have been tailored to produce crystalline indium nitride using lithium amide. Indium nitride is a very difficult material to synthesize and crystallize as a bulk powder because of its low decomposition temperature of 990 K.[22,23] Many different approaches had been attempted previously using solid-state metathesis reactions

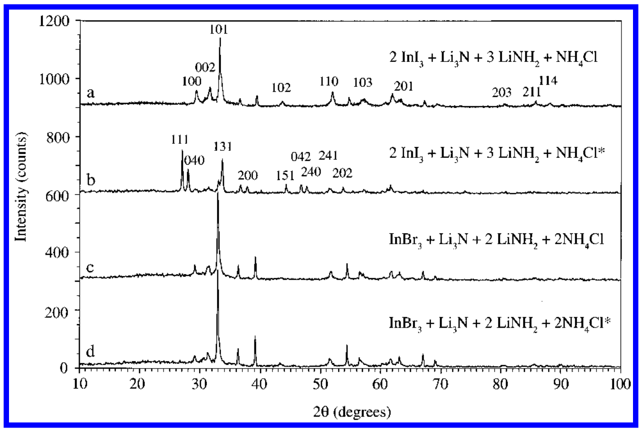

Figure 5. Powder X-ray diffraction patterns of InN produced by solid-state metathesis reactions at ambient pressure. The patterns labeled with an (*) were performed in the thermal dissipation cell. The Miller indices for InN are assigned on the top pattern. The Miller indices for InI are assigned on pattern 2. All unassigned peaks are due to In metal. The crystallinity of InN produced from InI_3 (a and b)- and $InBr_3$ (c and d)-containing reactions is comparable. InI_3 reactions had relatively low yields, while reactions involving $InBr_3$ had higher yields.

to produce crystalline indium nitride. The first reactions involved high pressure, which had been successful in the SSM synthesis of GaN, but even reactions at 6.0 GPa failed to produce crystalline InN from InI_3 and Li_3N. After the discovery that ammonium chloride enabled the formation of GaN at ambient pressures, a survey of reactions was carried out to produce InN. The molar ratios of the reactants were varied, yet all of the reactions produced only In metal or $In(OH)_3$ after the products were washed in water. By using lithium amide in conjunction with ammonium chloride, the synthesis of crystalline indium nitride via SSM reactions has been successful, as reported in Table 2.

An optimal ratio of precursors to produce InN using a metathesis reaction at ambient pressure is given in eq 4.

$$2InI_3 + Li_3N + 3LiNH_2 + NH_4Cl \rightarrow 2InN + 6LiI + 3NH_3 + HCl \quad (4)$$

The final product was isolated with the same method used for GaN. This reaction has a yield greater than 83%, but powder X-ray diffraction indicates that crystalline InN along with some In metal is present (Figure 5a). The product is not as crystalline as the GaN produced using a similar process, but the fact that bulk crystalline InN is produced at ambient pressure is significant. The presence of In metal in the product is not surprising and it can be removed with repeated washing with a solution of iodine in tetrahydrofuran.

The thermal dissipation cell, which rapidly removes heat from a metathesis reaction, can potentially be utilized to increase the yield of InN. Using the precursor InI_3, the most crystalline InN was still produced with a 2:1:3:1 molar ratio of InI_3:Li_3N:$LiNH_2$:NH_4Cl. In view of the role of NH_4Cl and $LiNH_2$ in GaN reactions discussed previously, it appears that InI_3 (mp 483 K) performs an analogous role to NH_4Cl, i.e., excess InI_3 serves as a heat sink, lowering the overall reaction temperature and keeping the reaction within the stability region of InN. Using the thermal dissipation cell, the overall reaction yield after isolating the products with an ethanol wash is <50%. Powder XRD analysis indicates the presence of InN, InI, and In (Figure 5b). In essence, the thermal dissipation cell increased the yield of InI (mp 624 K) by lowering the reaction temperature and preventing the escape of InI_3 from the reaction mixture. With a boiling point of 984−988 K, InI is a stable byproduct which forms in preference to InN. To overcome the problems associated with InI_3, $InBr_3$ was used as a substitute. The use of bromides had been avoided in the past because LiBr formation generally results in a more exothermic reaction and subsequent decomposition of any InN product. However, the use of a thermal dissipation cell reduces this problem. It can be seen that the reaction consisting of a molar ratio of 1:1:2:2 $InBr_3$:Li_3N:$LiNH_2$:NH_4Cl results in the production of InN and In metal with no InBr contaminant (Figure 5c, 5d). The product yield is 27.6%; however, this includes some In metal. Experiments are in progress to avoid the formation of In and increase the yield of InN.

Conclusions

The use of lithium amide in solid-state metathesis reactions enables the formation of highly crystalline gallium nitride, in excellent yield, at ambient pressure. The most crystalline GaN forms when a slight excess of Li_3N-to-GaI_3 is used, i.e., a ratio of Li_3N:GaI_3:$LiNH_2$:NH_4Cl of 6:7:3:3. By combining this optimal reactant ratio with a specially designed thermal dissipation cell, yields of crystalline gallium nitride of up to 78.8% have been obtained. Lithium amide has proven to be a reactive nitrogen source. When it is used in conjunction with ammonium chloride, the reaction temperature is moderated, providing an optimal environment for the crystallization of gallium nitride. Indium nitride (decomposition temperature 990 K) is a material that is even more temperature sensitive than GaN (decomposition temperature 1150 K) and therefore difficult to crystallize. However, application of the techniques developed for the synthesis of crystalline GaN now enables crystalline InN to be produced by solid-state metathesis reactions.

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References and Notes

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