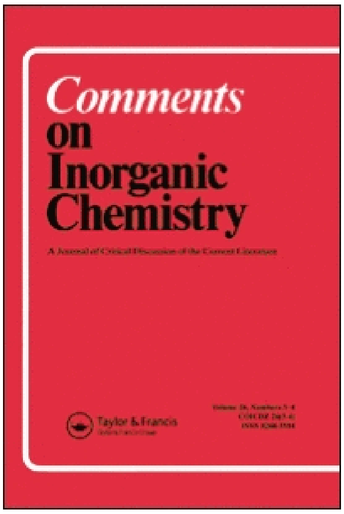

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Single Source Precursors to Group III (13) Metal Nitrides

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Single Source Precursors to Group III (13) Metal Nitrides

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A review of the preparation of single source precursors (SSPs) to the group III metal nitrides (aluminum nitride, gallium nitride and indium nitride) is given. The SSPs are divided into three categories (1) volatile small molecules for chemical vapor deposition studies, (2) polymeric precursors for the formation of fibers and thin films, and (3) compounds developed for the formation of small-particle powders. The methods for conversion of the SSPs into the desired nitrides and the analysis of the resulting nitride materials are given whenever possible.

Key Words: *aluminum nitride, gallium nitride, indium nitride, nitride films, chemical vapor deposition, single source precursor*

1. INTRODUCTION

Recently a great deal of interest has been shown in aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN). First, AlN is of interest since it is a hard and refractory material[1] (hardness between corundum and diamond, MP = 2400 °C), an electrical insulator[1] (band gap 5.9–6.2 eV), chemically inert[1] (stable in air up

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to 700 °C), and a piezoelectric material with a high acoustic velocity.[1] It also possesses a high intrinsic thermal conductivity[2,3] (80–200 W/mK in polycrystalline and 320 W/mK in single crystal samples), and a thermal expansion coefficient similar to that of silicon and gallium arsenide[3] (AlN: 3.5×10^{-6}/°C, Si: 3.4×10^{-6}/°C, and GaAs: 5.9×10^{-6}/°C). AlN's non-toxic nature combined with its thermal and electrical properties make it a good candidate for replacing BeO (thermal conductivity ~216 W/mK) as a heat dissipator in electronic applications.[4] Because of its hardness and thermal stability, AlN has been suggested as a potential protective coating for high temperature materials.[5] Finally, since it is a piezoelectric with a high acoustic velocity, it has been suggested for use in the fabrication of surface acoustic wave devices.[1] Second, interest in GaN is due to its direct band gap of 3.4 eV,[6] high ballistic electron drift velocity,[6,7] high acoustic velocity,[6,8] and piezoelectric properties.[6,8] Potential uses of GaN include visible and near UV light-emitting diodes,[6] blue semiconductor lasers,[6] high frequency and microwave power devices,[6,7] and acousto-optic applications.[6,8] Finally, InN is of interest due to its band gap of ~1.9 eV.[9] Potential applications for InN include optoelectronic devices operating in the visible range, low-cost solar cells, and electrochromic devices.[9]

Formation of the metal nitrides is accomplished by a variety of techniques. Traditionally, AlN and GaN have been produced by direct nitridation of the metal or via reaction of the metal oxide with a nitrogen source. Both of these methods require extreme temperatures, typically >900°C. InN, however, dissociates into its elements at temperatures as low as 300 °C under vacuum and, thus, is not produced via these traditional methods. Each of the group III metal nitrides can also be prepared via chemical vapor deposition (CVD) routes involving the reaction of either a metal halide or metal alkyl with a nitrogen source, separate source CVD.

Single source precursors (SSPs), containing both the metal and nitrogen atoms which will combine to form the metal nitride, can offer several advantages over the traditional methods and the separate source CVD routes. First, in theory, if the correct stoichiometric ratio of M to N is possessed by the SSP, then this ratio should be retained in the metal nitride produced from the SSP. The retention of this stoichiometry relies on the metal–nitrogen bond being strong enough to avoid scission under the experimental conditions employed to form the metal nitride. Secondly, the common precursors for most CVD routes to group III metal nitrides are a metal halide or metal alkyl and a nitrogen source, typically ammonia or hydrazine. The metal halides employed in these CVD processes eliminate, upon formation of the metal nitride, undesirable halide by-products, most commonly corrosive hydrogen halides. Many SSPs to group III metal nitrides do not contain metal halide bonds and, therefore, do not form these undesirable halide by-products. The metal alkyls normally employed in CVD processes are spontaneously flammable in air and often will react with oxygen, which may be adsorbed onto the reactor lines or walls, leading to the incorporation of oxygen as an impurity in the resulting metal nitrides. In contrast, SSPs containing metal nitrogen bonds are typically much less reactive towards oxygen and are, therefore, not as hazardous to handle, nor do they incorporate as many oxygen impurities into the final nitride. Thirdly, if designed properly, SSPs will contain substituents on the metal and nitrogen atoms which will be readily eliminated under the experimental conditions, therefore leading to the possibility of forming metal nitrides at temperatures significantly lower than those employed in other nitride-forming processes. Fourth, SSPs designed for CVD processes should provide uniform coverage of substrates of all shapes. Finally, SSPs can lead to a simplification of the CVD reactor, leading to an improvement in the integrity of the system and, therefore, lower levels of oxygen impurities.

The pursuit of SSPs to the group III metal nitrides has been for three general purposes: (1) the formation of films, at relatively low temperatures (<500 °C), via a CVD process, (2) the formation of films and fibers from polymeric precursors, and (3) the formation of nitride powders consisting of small particles (micron to submicron).

2. SSP SYSTEMS TO AlN

2.1 CVD Routes to Films of AlN

The first report of employing an SSP in a CVD route to form AlN utilized an aluminum trichloride ammonia complex, $AlCl_3{:}3NH_3$(**I**), formed by the room temperature reaction of aluminum trichloride with an excess of ammonia, followed by the sublimation of **I** at 350

°C in flowing ammonia.[1] The deposition of films of AlN, characterized by XRD, from **I** occurs at temperatures ranging from 800–1200 °C. This method of preparing AlN suffers from relatively high temperatures and the formation of corrosive hydrogen chloride as a by-product.

Another early attempt at producing AlN films from SSPs via CVD involved the investigation of $[HAl(NR_2)_2]_2$ (**II**) and $[Al(NR_2)_3]_3$ (**III**), where R = Me, Et as potential sources of AlN.[5] Compounds **II** and **III** are prepared as outlined below:

$$2\ H_3Al{:}NMe_3 + 4\ NR_2H \rightarrow [HAl(NR_2)_2]_2 + 4\ H_2 + 2\ NMe_3$$

$$3\ LiAl(NR_2)_4 + AlCl_3 \rightarrow 4\ Al(NR_2)_3 + 3\ LiCl$$

When compounds **II** and **III** are decomposed on a substrate at 300–500 °C, films of composition $AlC_{1.2}N_{0.4-0.6}O_{0.06-0.2}$ are obtained as analyzed by Auger electron spectra of the films etched to a depth of 300–500 Å. The surface analysis of the same films shows a composition of $AlC_{1.3}N_{0.05}O_{0.4}$, presumably due to oxidation or hydrolysis of the surface which occurs during handling in air. X-ray diffraction studies of the films obtained from **II** and **III** which were subsequently annealed at 1300 °C for 15 minutes reveal broad diffraction peaks which roughly correlate with those of AlN. Although these experiments do not produce pure AlN, they demonstrate that nitrogen is retained in the films upon thermal decomposition and that proper compound selection should lead to the use of SSPs as a route to AlN.

The next report of an attempt to employ SSPs in CVD to prepare AlN films presents studies employing dialkylaluminum amides, $(R_2AlNH_2)_x$ where R = Me, Et, *i*-Bu, and *t*-Bu.[2a] The most promising of these compounds is dimethylaluminum amide, $(Me_2AlNH_2)_3$ (**IV**), prepared as shown in the following reaction:

$$3\ AlMe_3 + 3\ NH_3 \xrightarrow{RT} 3\ Me_3Al{:}NH_3 \xrightarrow{>55\ ^\circ C} [Me_2AlNH_2]_3 + 3\ CH_4$$

Compound **IV** forms films of AlN (with oxygen content of 4–5%) when deposited at temperatures in the range 400–800 °C.[2b] Films prepared from **IV** possess optical and electrical properties consistent with those of AlN, and films prepared at or above 600 °C are optically transparent. A 1989 report describes the preparation of AlN films via CVD employing a series of compounds, $(Me_2AlN_3)_3$ (**V**), $(Et_2AlN_3)_3$ (**VI**), and $(Et_2AlNH_2)_3$ (**VII**),[10] whose syntheses are illustrated by the following reactions:

$$3\ [R_2AlCl]_2 + 6\ NaN_3 \rightarrow 2\ [R_2AlN_3]_3 + 6\ NaCl$$

where R = Me, Et

$$3\ AlEt_3 + 3\ NH_3 \rightarrow [Et_2AlNH_2]_3 + 3\ C_2H_6$$

Compounds **V**, **VI**, and **VII** are similar to those previously employed in the preparation of AlN films.[2] The composition of the AlN films obtained from deposition of **V**, **VI**, and **VII** at 500 °C are as follows (expressed in atom %): **V**: Al 35–47%, N 29–44%, C 7–11%, and O 2–9%; **VI**: Al 43–45%, N 42–45%, C 5–12% and O 2–8%; **VII**: Al 38–44%, N 24–41%, C 2–7%, and O 8–35%. Although **V**, **VI**, and **VII** yield AlN films, it is clear that the films obtained when **IV** is employed are of superior chemical composition, containing little carbon and only 4–5% oxygen.

Another precursor to AlN, technically not an SSP but containing Al–N bonds in the precursor molecule, $Al_2(NMe_2)_6$ (**VIII**), is worth mentioning since CVD employing **VIII** in an atmosphere of ammonia produces AlN films.[11] The deposition of AlN films with **VIII** can be conducted at 100–500 °C, offering the lowest temperature CVD route to AlN films. The films obtained from **VIII** possess an Al to N ratio of approximately one, can be grown at rates of 1000–1500 Å/min, contain no measurable carbon, and contain only 1–5 atom % of oxygen. However, these films contain from 37–18 atom % hydrogen when deposited at temperatures in the range 100–500 °C, respectively. The hydrogen content seems, however, to have only minor effects on the band gap of the deposited films, which ranges from 5.00 to 5.77 eV for films deposited at 100–500 °C, respectively. It seems clear from the lack of measurable carbon that the nitrogen contained in the precursor **VIII**, which contains bonds to carbon, is not the nitrogen which is incorporated into the films. A transamination reaction is presumed to occur as idealized in the following reaction:

$$Al_2(NMe_2)_6 + 6\ NH_3 \rightarrow \text{“}Al_2(NH_2)_6\text{”} + 6\ NMe_2H$$

2.2 Polymer Routes to Films and/or Coatings of AlN

Three distinctly different routes to processable polymeric precursors to AlN have been reported.[12-14] The first route, reported in 1987, involves the synthesis of polymers (**IX**) as illustrated by the following reaction, conducted at 140–175 °C[12]:

$$(R_2AlNH_2)_x + n\ AlR'_3 \rightarrow \text{polymers } \mathbf{IX}$$

$x = 2$ or 3; $R = C_yH_{2y+1}$ where $y = 1 - 10$; $R' = C_yH_{2y+1}$ where $y = 1 - 10$; $n = 0.002$–0.500. Polymers **IX** prepared by the above reaction can be spun into fibers or formed into shapes. Subsequently **IX** can be cured into an infusible form by exposure to ammonia or hydrazine. The cured **IX** can then be pyrolyzed to AlN at temperatures in the range 800–1000 °C in the presence of ammonia or hydrazine. The AlN thus produced can subsequently be densified by heating to 1800 °C. Although the temperatures employed in this process are quite high, it offers an excellent route to fibers, tapes, and films of AlN.

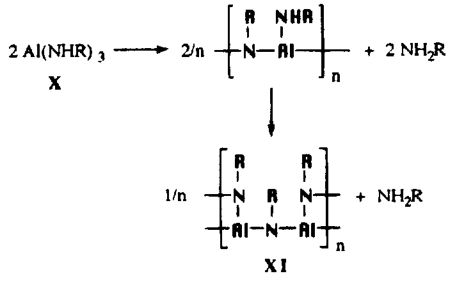
The second route employs the electrochemical synthesis of $Al(NHR)_3$ (**X**) and its subsequent condensation to a polymer of formula $Al(NR)_{1.5}$ (**XI**), where $R = n\text{-}C_3H_7$.[13] The sequence of reactions presumed to be involved in the electrochemical synthesis of **X** is shown in the following reactions:

$$2\ Al \rightarrow 2\ Al^{3+} + 6e^- \quad \text{anode half reaction}$$

$$6\ NH_2R + 6e^- \rightarrow 6\ NHR^- + 3\ H_2 \quad \text{cathode half reaction}$$

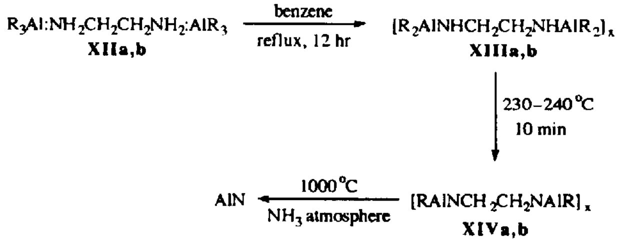
$$2\ Al + 6\ NH_2R \rightarrow 2\ Al(NHR)_3 + 3\ H_2 \quad \text{overall reaction}$$

The condensation of **X** to **XI** is illustrated in the following reaction scheme:



Pyrolysis of **XI** in an ammonia atmosphere produces bulk crystalline AlN at temperatures as low as 850 °C. The purity of the AlN obtained is highly dependent upon the atmosphere in which the pyrolysis is performed. An atmosphere of ammonia leads to the purest AlN (0.8% C, 2.5% O), nitrogen yields AlN contaminated by 1.6% carbon and 9.1% oxygen, and argon produces low purity AlN (25.0–28.3% C, 1.8–2.2% O), percentages expressed as weight %. Coating of SiC fibers with **XI** followed by pyrolysis at 900 °C results in nearly continuous coatings of AlN.[13b]

The third route utilizes the reactions of ethylenediamine with trimethyl- and triethylaluminum in 1:2 stoichiometric ratios (amine to aluminum alkyl) to obtain processable polymers, **XIIIa,b**.[14a] Other ratios of ethylenediamine to aluminum alkyl have also been attempted; however, the 1:2 ratio produces the best results.[14] The reaction sequences leading to the formation of AlN from the reactions of 1:2 stoichiometry of ethylenediamine to aluminum alkyl are illustrated below:



a: R = Et and b: R = Me

Products **XIVa,b** are glassy solids insoluble in hydrocarbon solvents; however, when pyrolyzed in an ammonia atmosphere at 1000 °C, both yield AlN as identified by XRD. Product **XIIIa** is soluble in benzene or toluene, which allows films to be formed on substrates, whereas product **XIIIb** is insoluble in hydrocarbon solvents. Films of AlN are formed on a silicon substrate by dropping a solution of **XIIIa** onto the substrate, evaporating the solvent, and pyrolyzing the resulting film of **XIIIa** in an ammonia atmosphere at 900 °C. The film thus obtained possesses an aluminum to nitrogen ratio of approximately one and contains 4.6 and 5.3 atom % of carbon and oxygen, respectively. Product **XIIa** is unstable at room temperature and must be stored at temperatures of -10 °C or less.

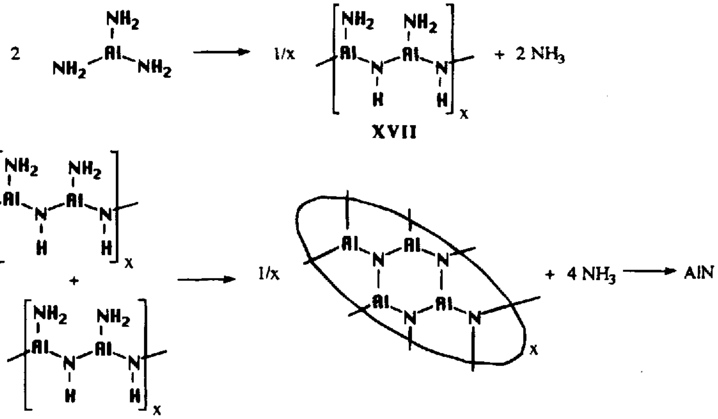
Reactions of trimethyl- and triethylaluminum with ethylenediamine in a 3:2 stoichiometric ratio yield the novel compounds $RAl[(HN(CH_2)_2NH)AlR_2]_2$ (**XVa,b**), where a: R = Et, and b: R = Me.[14b] The controlled pyrolysis of **XVa,b** to glassy solids is reported. The glassy solids thus obtained are found to be slightly soluble in hydrocarbon solvents. The formation of AlN from **XVb** pyrolyzed in a stream of ammonia is mentioned; however, it appears that the low solubility of **XVb** renders it unprocessable and thus uninteresting as an SSP to AlN film.

2.3 Routes to Bulk AlN

A polymer, of composition $[Al(NH_2)NH]_x$ (**XVI**), formed by the room temperature condensation of $Al(NH_2)_3$, produces bulk AlN when pyrolyzed at elevated temperatures.[15] The $Al(NH_2)_3$ used as a precursor to **XVI** is formed in liquid ammonia by the following reaction:

$$AlBr_3 + 3\ KNH_2 \rightarrow Al(NH_2)_3 + 3\ KBr$$

An electrochemical route which utilizes aluminum electrodes and NH_4Br as an electrolyte in liquid ammonia produces a mixture of a polymer, composition $[Al(NH_2)NH]_x$ (**XVII**), and $Al(NH_3)_6Br_3$.[16] Polymer **XVII** is believed to be similar to the previously reported polymer **XVI**.[15] Spectroscopic evidence suggests that the aluminum atoms in **XVII** are six coordinate, indicating complexation with ammonia. The pyrolysis of mixtures of **XVII** and $Al(NH_3)_6Br_3$ in an ammonia atmosphere results in the formation of AlN at temperatures as low as 600 °C. The $Al(NH_3)_6Br_3$ preferentially sublimes from the mixture at temperatures $\leq$ 400 °C. The AlN obtained from the pyrolysis of **XVII** is quite pure (elemental analysis found: Al 66.12%; N 33.92%; O 1.4%; C < 0.5%; Br < 0.5%; H < 0.5%, elemental analysis calculated: Al 65.9%; N 34.1%). The primary particle diameter and mean crystallite diameter of AlN formed by heating a mixture of **XVII** and $Al(NH_3)_6Br_3$ to 1100 °C in an ammonia atmosphere are 0.024 and 0.012 μm, respectively. Although this route suffers from the use of a halogen containing compound, it is an excellent route to small-particle powders of AlN. The formation of **XVI** and **XVII** from $Al(NH_2)_3$ and their conversion to AlN are illustrated below:



XVII

The production of bulk AlN from $[Cl_2AlNHSiMe_3]_2$ (**XVIII**) has also been reported.[3] Compound **XVIII** is formed from the reaction of $AlCl_3$ with $HN(SiMe_3)_2$. The reaction sequence for the formation of AlN from these reactants is illustrated by the following three reactions:

$$AlCl_3 + HN(SiMe_3)_2 \xrightarrow{60\,^{\circ}C} 1/2\ \underset{\textbf{XVIII}}{[Cl_2AlNHSiMe_3]_2} + SiMe_3Cl$$

$$1/2\ [Cl_2AlNHSiMe_3]_2 \xrightarrow{T \geq 200\,^{\circ}C} 1/n\ [ClAlNH]_n + SiMe_3Cl$$

$$1/n\ [ClAlNH]_n \xrightarrow{T \geq 500\,^{\circ}C} AlN + HCl$$

The AlN obtained by pyrolysis of **XVIII** at temperatures ≥ 1100 °C in an argon or ammonia atmosphere contains significant oxygen and silicon impurities. The AlN obtained by pyrolysis of **XVIII** at temperatures of 1000 °C in an argon or ammonia atmosphere contains significant chlorine impurities along with those of oxygen and silicon. The elemental analyses of the AlN obtained from **XVIII** under various pyrolysis conditions are N 26.3–28.3%; O 6.4–9.4%; Cl $\leq$ 0.1–6.2%; Al 48.2–54.3%; Si 1.4–7.9%; C 0.10–0.27% (percentages by weight %). The AlN obtained by pyrolysis of **XVIII** in an argon atmosphere at 1000 °C consists of amorphous plates ranging in size from 100 to 200 μm.

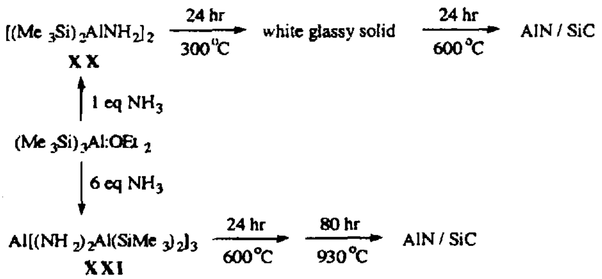
Recently, $AlH_3(NMe_3)_2$ (**XIX**) has been employed as an SSP to bulk AlN.[17] Compound **XIX** is prepared by the following reaction conducted in ether:

$$LiAlH_4 + NMe_3HCl + \text{xs } NMe_3 \rightarrow AlH_3(NMe_3)_2 + LiCl + H_2$$

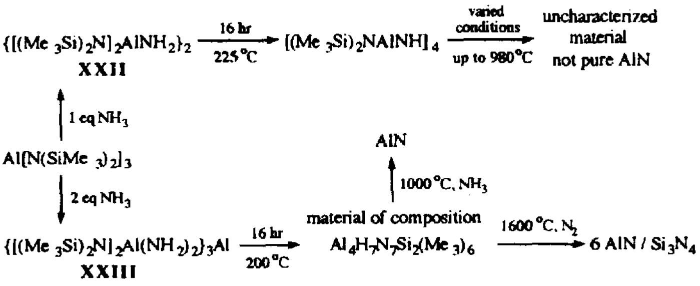
Treatment of **XIX** with ammonia at room temperature yields a white solid postulated to be **XVII**. Pyrolysis of **XVII**, obtained from **XIX**, at 1100 °C in an ammonia atmosphere results in high purity AlN (C $< 0.3\%$) consisting of particles ~0.5 μm in size. Although the particles of AlN obtained from **XIX** are not as small as those obtained from mixtures of **XVII** and $Al(NH_3)_6Br_3$, **XIX** contains no halogen atoms and produces only trimethylamine and hydrogen as by-products. Therefore, if 0.5 μm particles of AlN are small enough for a particular application, then **XIX** is the precursor of choice.

2.4 Related Studies

The syntheses of $[(Me_3Si)_2AlNH_2]_2$ (**XX**) and $[(Me_3Si)_2Al(NH_2)_2]_3Al$ (**XXI**) and their conversion to AlN/SiC composites have been reported.[18] The authors speculate that the weaker silicon–aluminum bonds in **XX** and **XXI**, relative to silicon–carbon bonds, will react more readily with acidic N–H groups, thereby forming AlN at lower temperatures than the corresponding aluminum alkyls and without carbon impurities. The AlN/SiC composites produced from **XX** and **XXI** contain approximate aluminum to silicon ratios of 2:1 and 5:1, respectively. Although **XX** and **XXI** do not yield pure AlN, the authors state that there may be some benefit to forming the composites.[18] Reaction sequences illustrating the conversion of **XX** and **XXI** to AlN/SiC composites appear below:



Another set of compounds containing the trimethylsilyl group, $\{[(Me_3Si)_2N]_2AlNH_2\}_2$ (**XXII**) and $\{[(Me_3Si)_2N]_2Al(NH_2)_2\}_3Al$ (**XXIII**), and their pyrolyses to ceramic materials have been reported.[19] The syntheses of **XXII** and **XXIII** and the results of the pyrolysis studies are illustrated below:



Compound **XXII** is not a useful precursor to AlN; however, upon pyrolysis **XXIII** forms AlN or AlN/Si_3N_4 composites, depending upon the pyrolysis atmosphere (see above scheme).

3. SSP SYSTEMS TO GaN

3.1 CVD Routes to h-GaN

The first report of employing an SSP in a CVD route to form h-GaN utilizes a gallium tribromide ammonia complex, $GaBr_3{:}4NH_3$ (**XXIV**), formed by the interaction of molten $GaBr_3$ with an excess of ammonia, followed by distillation of **XXIV** in an atmosphere of ammonia.[20] The deposition of films of h-GaN, characterized by reflection electron diffraction, occurs at 600 °C and 750 °C in atmospheres of ammonia and nitrogen or argon, respectively. Higher deposition temperatures result in the contamination of the films by gallium metal. Although the temperatures employed in this process are moderate, it suffers from the fact that **XXIV** contains bromide, which likely generates corrosive hydrogen bromide as a by-product.

The second report involves the growth of h-GaN thin films from "triethylgallium monoamine (**XXV**)," most likely diethylgallium amide.[21] Deposition of h-GaN, characterized by XRD and reflection electron diffraction, from **XXV** is accomplished at temperatures in the range 600–800 °C in a nitrogen atmosphere, with growth rates of 0.5–2.0 μm/hr.

The third report involves the growth of high purity h-GaN from $[Et_2GaN_3]_3$ (**XXVI**).[22] Compound **XXVI** is prepared by the following reaction:

$$3\ Et_2GaCl + 3\ NaN_3 \rightarrow [Et_2GaN_3]_3 + 3\ NaCl$$

High purity films of h-GaN ($< 2\%$ O, $< 2\%$ C, atom %) are formed from **XXVI** by deposition at an optimum temperature of 350 °C followed by annealing at 600 °C. These films are deposited at rates of 0.015–0.050 μm/min. The carbon and oxygen content is determined by Auger spectroscopy and the gallium to nitrogen ratio (~ 1) is determined by Rutherford backscattering and electron microprobe analysis. Deposition of h-GaN films from **XXVI** at lower temperatures results in higher oxygen content (> 5 atom %), while deposition at higher temperatures results in an increase in carbon content (~ 10 atom % for films deposited at 450 °C). The h-GaN films deposited from **XXVI** at 350 °C contain significant quantities of hydrogen, probably in the form of gallium–hydrogen bonds, and are thus sensitive to air oxidation. Therefore, annealing the films at 600 °C is necessary to eliminate this hydrogen content and render the films air stable. Additionally, the use of **XXVI** in the preparation of films of h-GaN has been explored by another group of investigators,[10d] who find that amorphous-polycrystalline h-GaN is formed from **XXVI** at deposition temperatures in the range 400–600°C.

The use of $Ga_2(NMe_2)_6$ (**XXVII**) as a precursor to h-GaN, which requires ammonia as the source of nitrogen, although technically not an SSP, merits mention since films are deposited at temperatures in the range 200–400 °C.[11a,c]

3.2 Production of Bulk c-GaN

The first example of a procedure to obtain bulk c-GaN is an SSP procedure. The compound, $(H_2GaNH_2)_3$ **(XXVIII)**, is converted to crystalline c-GaN at temperatures as low as 180 °C with complete crystallinity observed at 600 °C. **XXVIII** is prepared as shown in the following reaction[23,10c]:

$$3\ Me_3N{:}GaH_3 + xs\ NH_3 \rightarrow (H_2GaNH_2)_3 + 3\ H_2 + NMe_3$$

Elemental analysis suggests the formula $GaN_{0.83}$ for the c-GaN produced, with carbon and hydrogen both less than 0.5 weight %. The c-GaN slowly converts to h-GaN with 50% conversion after 120 hr at 900 °C.

3.3 Related Studies

Two other studies with goals of producing GaN from SSPs have been reported. The use of the Lewis acid–base adduct $Cl(Et)_2Ga{:}NEt_3$ **(XXIX)** to form GaN leads instead to the formation of gallium droplets and free NEt_3.[24] On changing the reaction conditions, "a non-uniform polycrystalline layer containing gallium and nitrogen"[24] is obtained; however, no further characterization is given. Another investigation reports the synthesis of three Lewis acid–base adducts of trineopentyl gallium, $Np_3Ga{:}NH_3$, $Np_3Ga{:}NMe_2H$, and $Np_3Ga{:}N(t\text{-}Bu)H_2$ where Np = neopentyl, each of which dissociates the amine upon thermolysis.[25]

4. SSP SYSTEMS TO InN

4.1 SSP to Bulk InN

The formation of InN from the thermolysis of $In(NH_2)_3$ **(XXX)** and $Na_xIn(NH_2)_{3+x}$ **(XXXI)**, where x = 1–3, has been reported.[26] Compounds **XXX** and **XXXI** are prepared in liquid ammonia as outlined by the following reactions:

$$InI_3 + 3\ KNH_2 \rightarrow In(NH_2)_3 + 3\ KI$$

$$InI_3 + (3 + x)\ NaNH_2 \rightarrow Na_xIn(NH_2)_{3+x} + 3\ NaI$$

where x = 1–3. The thermolysis of **XXX** at 207 °C under vacuum followed by thermolysis of the resulting product at 415 °C under 1 atmosphere of nitrogen produces InN (99% yield) as identified by XRD. Thermolysis of **XXXI** at 360 °C in a nitrogen atmosphere produces, after ethanol and water washes, InN (20%) identified by XRD and elemental analysis. This is the first report of an SSP to be employed in the successful synthesis of InN.

4.2 Related Studies

Two studies related to the preparation of InN from SSPs have been reported. The pyrolysis of $[Me_2InNEt_2]_2$ at 400 °C in vacuo produces pure indium metal.[27] This result is not surprising since InN is reported to be unstable in vacuo above 300 °C.[28] Another study reports the synthesis of $(Me_2InNH_2)_x$ (**XXXII**).[29] Compound **XXXII** is formed from $Me_3In{:}NH_3$, which slowly undergoes thermal decomposition at room temperature with the release of methane. The formation of **XXXII** is accelerated by heating to 70–80 °C. Compound **XXXII** is reported to melt at 120–124 °C with further decomposition forming a thick syrup; however, no further description or characterization of the decomposition product is given.

5. CONCLUDING REMARKS

Interest in AlN, GaN and InN has been generated by the potential for exploiting their physical properties in electronic applications. Recent studies have focused on the use of SSPs to form thin films, fibers, and bulk powders of these materials. In the last 8–10 years great progress has been made in producing SSPs to AlN. The challenges of producing AlN films at relatively low temperatures (< 500 °C) have been met,[2,10,11] with deposition temperatures as low as 100 °C reported.[11] Polymeric precursors to AlN which can be fabricated into various shapes and made into composites have also been produced,[12-14] as well as pure powders of AlN, which consist of submicron particles.[16,17] The current challenge is to incorporate the chemistry thus far developed for AlN into the production of useful devices and into practical applications. In the case of GaN, films of h-GaN have been produced from SSPs at temperatures as low as

200 °C.[10d,11a,c,22] However, the unexpected finding is the formation of c-GaN at temperatures as low as 180 °C.[10c,23] It will be of interest to see if thin films of c-GaN can be produced in the future by a CVD or polymer route. Although InN has been prepared in bulk from an SSP,[26] the preparation of films from an SSP has not yet been reported. It would seem that a reinvestigation of the decomposition chemistry of **XXXII** is worthwhile and might lead to a polymeric SSP to InN.[29] Finally, solutions of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ have been prepared by various non-SSP routes, and their band gaps have been found to vary linearly with x.[30,31] Such solutions have potential applications for use in light emitting diodes and lasers, operating from the orange (2 eV) to the UV (6 eV).[30,32] No SSPs to these solutions have yet been reported; therefore, an extension of the SSP concept to the formation of these solutions seems merited.

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