Reviews

Growth of Group III Nitrides. A Review of Precursors and Techniques

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The AlGaInN quaternary alloy system is uniquely suited for numerous device applications because the bandgap can be varied from 1.9 to 6.2 eV by changing the alloy composition. Growth of epitaxial device-quality group III (Al, Ga, In) nitride films has been hindered by a lack of suitably lattice matched substrates, the large equilibrium dissociation pressure of N_2 from the nitrides at typical growth temperatures, and predeposition reactions in the commonly employed metal−organic chemical vapor (MOCVD) precursors. The most successful films have been grown at temperatures in excess of 900 °C by MOCVD. However, high growth temperatures may limit compatibility and incorporation of group III nitrides with existing fabrication technologies and devices. Attempts to lower deposition temperature include activated nitrogen sources and alternative precursors. This review will discuss improvement in film properties as a function of growth chemistry and will focus on MOCVD precursors used specifically for the growth of group III nitrides.

Introduction

The refractory group III nitrides (group III refers to Al, Ga, In) are the focus of intense research and device development.[1] The wurtzite polytypes of gallium nitride (GaN), aluminum nitride (AlN), and indium nitride (InN) are excellent materials for bandgap engineering, because they form a continuous range of solid solutions and superlattices with direct room-temperature bandgaps ranging from 1.9 eV for InN, to 3.4 eV for GaN, to 6.2 eV for AlN (Figure 1).[2] The group III nitrides are ideal for high-power applications and utilization in caustic environments, because they are chemically inert, are resistant to radiation, and have large avalanche breakdown fields, high thermal conductivities, and large high-field electron drift velocities. The group III nitrides and their alloys have been fabricated into various high-temperature and high-power microelectronic and optoelectronic devices such as passivation barriers,[3] ohmic contacts[4] in integrated circuits, blue light-emitting diodes,[5] candela-class blue-light emitting diodes,[6] green and yellow light-emitting diodes,[7] UV photodetectors,[8] reflector stacks,[9] high electron mobility transistors,[10] heterostructure field effect transistor,[11] metal semiconductor field-effect transistors,[12] and surface acoustic wave devices.[13] Stimulated emission has been reported from optically pumped GaN[14] and AlGaInN alloy[15] double heterostructure films.

Growth of epitaxial device quality group III nitride films with low defect densities and dopant concentrations has been hindered by a lack of suitably lattice matched substrates, large *n*-type background carrier

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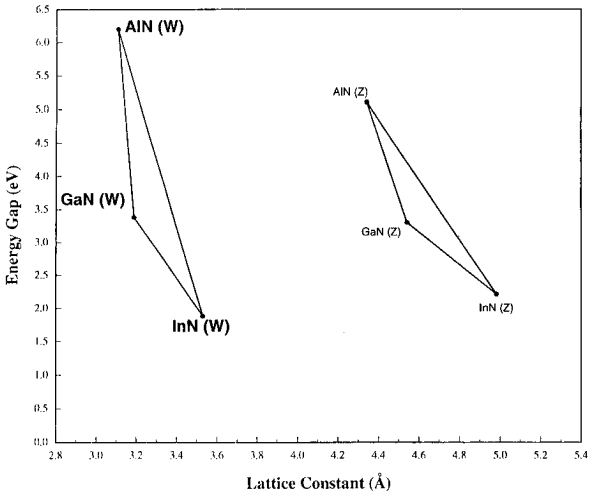

Figure 1. Bandgap versus lattice parameters for wurtzitic and cubic group III nitrides.

concentrations in the deposited nitride films, large equilibrium dissociation pressure of N_2 from the nitrides at typical growth temperatures, and predeposition reactions in the commonly employed metal−organic chemical vapor deposition (MOCVD) precursors, trimethylaluminum, trimethylgallium, or trimethylindium and ammonia. All studies before 1987 reported the fabrication of material that typically contained a large free electron concentration ($10^{19}-10^{20}$ cm^{-3}) and low mobility (10−20 cm^2/Vs). Recent advances in heteroepitaxial growth of thin films has resulted in significant improvements in crystallinity, electrical, and optical properties and the fabrication of practical devices. The successful use of buffer layers has allowed single-crystalline growth on poorly lattice matched substrates. The most successful films have been grown at temperatures in excess of 900 °C by MOCVD. However, the disadvantages associated with such high growth temperatures include introduction of thermal stresses in the films, accumulation of defects at the interface, poor compatibility with existing integrated circuit technology, and difficulty of indium alloy formation. Attempts to lower deposition temperature include activated nitrogen sources and alternative precursors. This review will discuss improvement in film properties as a function of growth chemistry and will focus on MOCVD precursors used specifically for growth of group III nitrides.

Structure of AlN, GaN, and InN

GaN is known to exist in at least two distinct crystalline polymorphs. They are the hexagonal equilibrium wurtzite structure (a) and the metastable cubic zinc blende structure (b) (Figure 2). A third polymorph

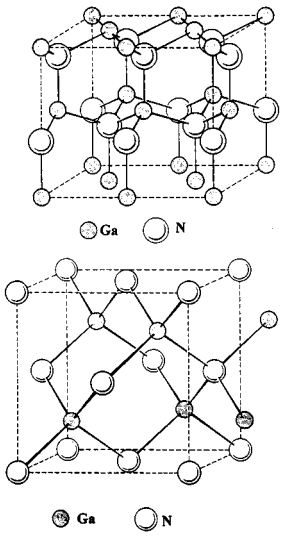

Figure 2. (a) Wurtzite structure of GaN. (b) Zinc blende structure of GaN. Reprinted with permission from *Introduction to Ceramics*, 2nd ed.; Kingery, W. D., Bowen, H. K., Uhlman, D. R., Eds.; John Wiley & Sons: Inc., New York, 1976.

is only formed under high pressure.[16] Both wurzitic and zinc blende GaN have tetragonal coordination with each atom bonded to four other atoms of opposite species. The nature of the bonding is predominately covalent with some ionic character. Wurzitic GaN is hexagonal close packed with an ABAB layer structure, and zinc blende GaN is cubic close-packed with an ABCABC layer structure. The nearest-neighbor positions are almost identical. Only the relative positions of the second nearest neighbor differ. The major difference between the two structures is the stacking order of the tetrahedral atomic sheets along the (111) axis. The wurtzitic hexagonal phase has lattice constants of $a = 3.186$ Å and $c = 5.178$ Å and a Ga−N bond length of 1.98 Å.[17] The zinc blende cubic phase has a lattice constant of 4.51 Å.[17] AlN and InN are most commonly observed in the wurzitic form with lattice constants of $a = 3.112$ Å, $c = 4.982$ Å and $a = 3.548$ Å, $c = 5.760$ Å, respectively, but AlN and InN can nucleate in the zinc blende phase[18] with lattice constants of 4.38 and 4.98 Å, respectively.

The wurtzite (0002) and zinc blende (111) stacking planes have the same lattice spacing. The wurtzite $(11\bar{2}0)$ and zinc blende (110) lattice spacings are also equal. Because the wurtzite and zinc blende structures differ only in their packing sequences, care must be taken when determining epitaxial growth by X-ray diffraction.[19]

Thermal Stability of Group III Nitrides

The group III nitrides thermally dissociate with loss of nitrogen near their melting points. The stability

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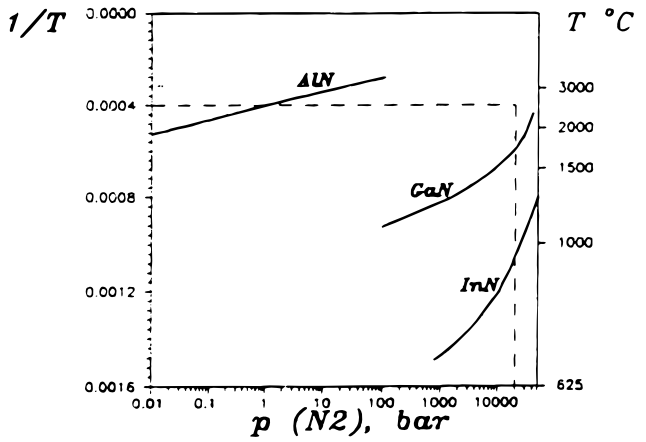

Figure 3. Stability limits for AlN, GaN, and InN. Reprinted with permisson from ref 20. Copyright 1993 Elsevier Science.

limits for AlN, GaN, and InN are presented in Figure 3.[20] AlN is significantly more thermally stable than GaN or InN. InN is the least stable group III nitride and is known to thermally dissociate at temperatures >600 °C. Even though stability at high temperatures is essential for use in high-temperature and high-power electronic and optoelectronic systems, few annealing studies of group III nitride films have been conducted. Thermal anneals of GaN indicated no decrease in photoluminescence intensity[21] or change in crystalline quality and electrical properties were observed for high-quality GaN films annealed at 900 °C under nitrogen. However, thermal decomposition was observed during a H_2 anneal at 900 °C. Hydrogen was proposed to reduce Ga^{3+} to gallium metal ($GaN + {}^3/_2H_2 \rightarrow Ga^0 + NH_3$).[22] Because of AlN's high melting point and low nitrogen dissociation pressure, similar results for AlN and AlGaN films would be expected. In contrast, InN is significantly less stable than AlN or GaN. Annealing InN films above 550 °C has been shown to severely degrade the film crystallinity. The degradation of the InN film is attributed to decomposition of the nitride with subsequent desorption of nitrogen. ($InN \rightarrow In^0 + {}^1/_2N_2$).[23]

Heteroepitaxial Growth of Group III Nitrides

Heteroepitaxial growth of group III nitrides on various substrates has been hindered by a lack of suitably lattice matched substrates, large equilibrium dissociation pressure of N_2 from the nitrides at typical growth temperatures, poor cracking efficiency of ammonia, and predeposition reactions in the commonly employed MOCVD precursors, trimethylaluminum, trimethylgallium, or trimethylindium with ammonia.[24] A combination of buffer layers, high growth temperatures (~700−1400 °C), activated nitrogen species, and large nitrogen source overpressures have been used to overcome these difficulties and obtain device quality films.

Table 1. Characterization Data for GaN Films Grown with Trimethylgallium and Ammonia at Substrate Temperatures of 775, 875, and 1050 °C[25]

	growth temp (°C)		
	775	875	1050
n (300 K) cm^{-3}	2×10^{19}	7×10^{17}	1×10^{17}
μ (300 K) cm^2/V s	69	148	350
μ (180 K) cm^2/V s	64	182	435
μ (77 K) cm^2/V s	56	88	254
PL (fwhm) (300 K) meV	160	80	25
abs edge (10−90%) nm	15	10	5

Growth of group III nitrides by MOCVD requires a minimum deposition temperature to provide sufficient mobility of surface species during growth to obtain epitaxial, single-crystalline growth of the group III nitrides. The conventional MOCVD precursor used for GaN growth, trimethylgallium, begins pyrolyzing at 475 °C, and oriented (0001) polycrystalline GaN has been deposited at 500 °C with ammonia and trimethylgallium. However, temperatures in excess of 800 °C are necessary to obtain single-crystalline high-quality GaN films on sapphire. The GaN films with the best electrical and optical properties are grown at 1050 °C (Table 1).[25] At substrate temperatures exceeding 1100 °C the dissociation of GaN results in voids in the growth layer. A similar temperature dependence is observed for AlN film growth by MOCVD. Although, trimethylaluminum is more reactive than trimethylgallium and begins pyrolyzing at 300 °C and oriented polycrystalline AlN is deposited at 400 °C, a minimum temperature of 1200 °C is necessary to obtain high-quality single-crystalline AlN on sapphire.[26] Disadvantages associated with high growth temperatures include introduction of thermal stresses in the films, accumulation of defects at the interface, dopant and impurity diffusion, poor compatibility with existing integrated circuit technology and difficulty of indium alloy formation.

New MOCVD deposition technologies utilizing an activated form of nitrogen[27] have attempted to lower deposition temperatures of group III nitride films. However, low growth temperatures often results in amorphous or polycrystalline materials, because there is insufficient energy for the adsorbed species to migrate to their preferred crystalline location. For example, polycrystalline and amorphous GaN[28] and AlN[29] have been deposited at temperatures <350 °C by plasma-enhanced CVD. Polycrystalline GaN has been deposited by combined laser and microwave plasma-enhanced chemical vapor deposition at 500 °C.[30] Better results have been obtained by activating the nitrogen source

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Table 2. Selected Physical Properties of Substrates for Group III Nitride Films[203]

substrate	sym	lattice parameters (Å)	CTE (10^{-6}/°C)	repeat unit GaN	repeat unit substrate	misfit with GaN (%)[a]
GaN	hexagonal	$a = 3.189$	5.59			
		$c = 5.185$	3.17			
GaN	cubic	$a = 4.52$	n/a[b]			
AlN	hexagonal	$a = 3.112$	4.2	a, hex	a	2.5
		$c = 4.982$	5.3	c, hex	c	4.1
AlN	cubic	$a = 4.38$	n/a	a, cubic	a	3.2
InN	hexagonal	$a = 3.548$	4	a, hex	a	−10.1
		$c = 5.760$	3	c, hex	c	−10.0
InN	cubic	$a = 4.98$	n/a	a, cubic	a	−9.2
(0001)sapphire	hexagonal	$a = 4.7759$	7.5	a, hex	$\sqrt{3}/2a$	22.7
		$c = 12.991$	8.5	$\sqrt{3}a$, hex	a	13.8
6H−SiC	hexagonal	$a = 3.08$	n/a	a, hex	a	3.5
		$c = 15.12$		c, hex	$1/3c$	2.9
ZnO	hexagonal	$a = 3.252$	2.9	a, hex	a	−1.9
		$c = 5.213$	4.75	c, hex	c	−0.54
Si(111)	cubic	$a = 5.4301$	3.59	$\sqrt{3}a$, hex	a	1.7
				c, hex	a	−4.5
GaAs(111)	cubic	$a = 5.6533$	6	$\sqrt{3}a$, hex	a	−2.3
				c, hex	a	−8.3
3C-SiC	cubic	$a = 4.36$	n/a	a, cubic	a	3.7
				a, hex	a	27
				c, hex	a	19
MgO	cubic	$a = 4.216$	10.5	a, cubic	a	7.2
				a, hex	a	24
				c, hex	a	23
$MgAl_2O_4$	cubic	$a = 8.083$	7.45	a, cubic	$1/2a$	12
				a, hex	$1/2a$	21
				c, hex	$1/2a$	28

[a] Lattice Mismatch = $f = (d_{substrate} - d_{film})/d_{film}$. [b] n/a = not available.

by a variety of techniques such as laser-assisted chemical vapor deposition (LCVD),[31] remote plasma enhanced chemical vapor deposition (RPCVD),[32] atomic layer epitaxy (ALE) with NH_3[33] and N_2[34] cracked by a hot filament, catalytically decomposed ammonia,[35] photo-assisted chemical vapor deposition,[36] and electron cyclotron resonance plasma-assisted chemical vapor deposition.[37] However, more research is needed with these activated nitrogen sources to grow device quality films and devices at deposition temperatures <700 °C. Atomic layer epitaxy is the most promising of the lower growth temperature techniques. ALE is capable of cracking ammonia at temperatures lower than those required for MOCVD, because of the more active surface covered with Ga atoms or their monomethylgallium radicals. The ALE process allows the adsorbed species to migrate with a higher surface diffusion than obtained by MOCVD or molecular beam epitaxy (MBE).[38]

Growth of AlN has been reported by high-temperature processes in the range 1050−1250 °C by MOCVD and reactive molecular beam evaporation.[39] A few high-quality epitaxial films have been grown at lower temperatures (300−700 °C) by switched atomic layer epitaxy,[40] electron cyclotron resonance plasma assisted CVD,[41] reactive sputtering,[42] and pulsed laser deposition.[43]

Perhaps the largest barrier to growth of device quality GaN films has been the lack of good lattice-matched substrate materials. For heteroepitaxial growth of GaN, various single crystals have been used as substrates, e.g., Si, 6H−SiC,[44] 3C−SiC,[45] MgO,[46] ZnO,[124] GaAs, and sapphire.[47] Among these the sapphire substrates of different crystallographic orientations have been the most popular, but the large difference in lattice parameters and thermal expansion coefficient are major problems (Table 2). Although SiC substrates have smaller lattice mismatches, they are expensive and

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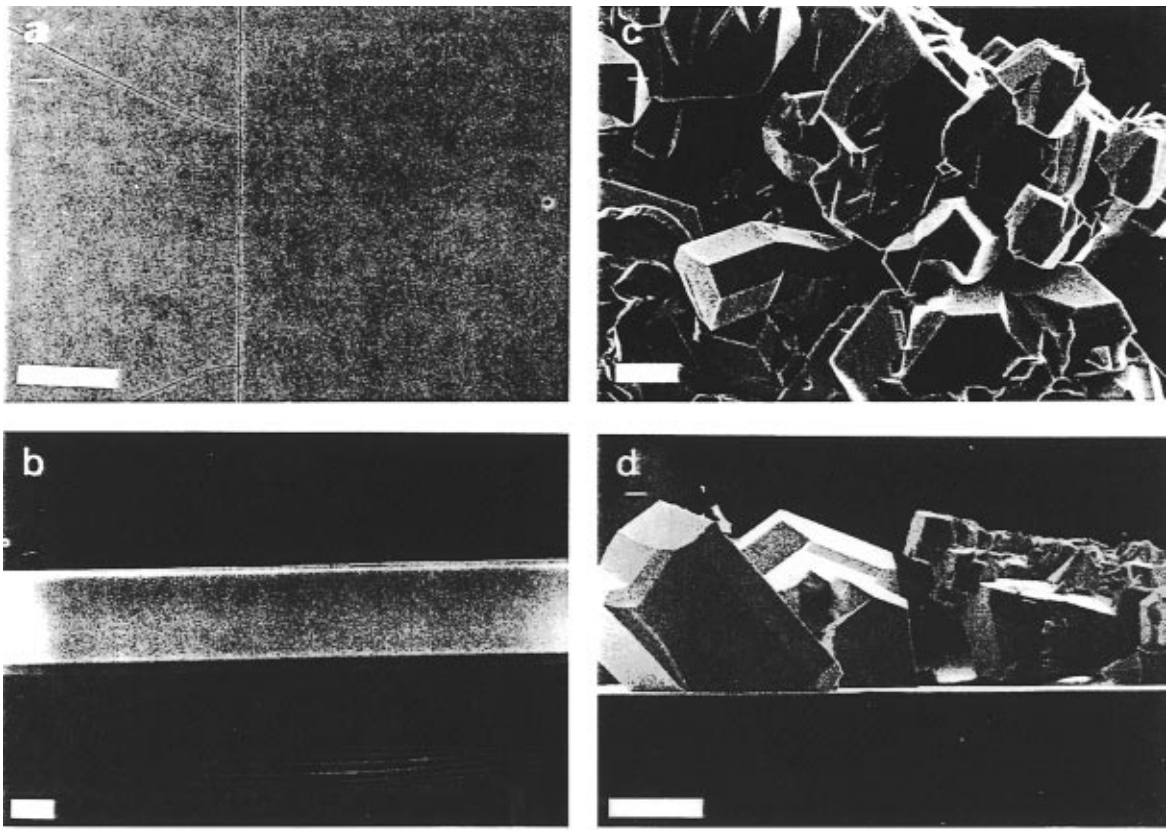

Figure 4. SEM photographs of the surface and cross sections of GaN films grown on Si substrates with (a), (b) and without (c), (d) AlN buffer layer. Markers represent (a) 5, (b) 1, (c) 5, and (d) 10 mm. Reprinted with permission from ref 51. Copyright 1993 Elsevier Science.

suffer from inferior structural quality compared to the commonly available sapphire wafers. Workers from Cree Research Inc. recently reported X-ray diffraction data with a fwhm of typical SiC substrates to be ~93 arc s[48] while sapphire fwhm's are routinely <10 arc s. Obtaining clean substrate surfaces prior to growth appears to be a major obstacle to the achievement of good-quality epitaxy.[49] Generally, growth of group III nitride films on poorly lattice matched substrates results in polycrystalline island-like films with poor surface morphology. The films are often cracked after post growth cooling as a result of thermal strain[50] as depicted for GaN growth on Si in Figure 4a.[51]

The use of buffer layers has dramatically improved crystallinity, film morphology, and electrical and optical properties. Examples include single-crystalline growth of GaN on AlN buffered (111) Si (Figure 4b, d),[51] GaN on AlN buffered sapphire,[52] GaN on GaN buffered sapphire,[53] InGaN alloys on GaN buffered (0001) sapphire,[54] AlGaN alloys on AlN buffered (0001) sapphire,[55] GaN and AlGaN alloys on Si with a 3C−SiC buffer layer,[56] thick GaN films (200−400 mm) by vapor phase epitaxy on sputtered ZnO buffered (0001) sapphire,[57] and InN films on AlN buffered (0001) sapphire.[58]

Using reactive molecular beam epitaxy, the growth of an AlN buffer layer was first shown to significantly improve the optical and electronic properties of the subsequent GaN layer.[52a,b] Three-dimensional growth of GaN by atmospheric pressure metal organic chemical vapor deposition (APMOCVD) on sapphire was shown to be effectively suppressed (Figure 5) by a two-step growth technique which uses either an AlN or GaN buffer layer grown at temperatures 400−600 °C before

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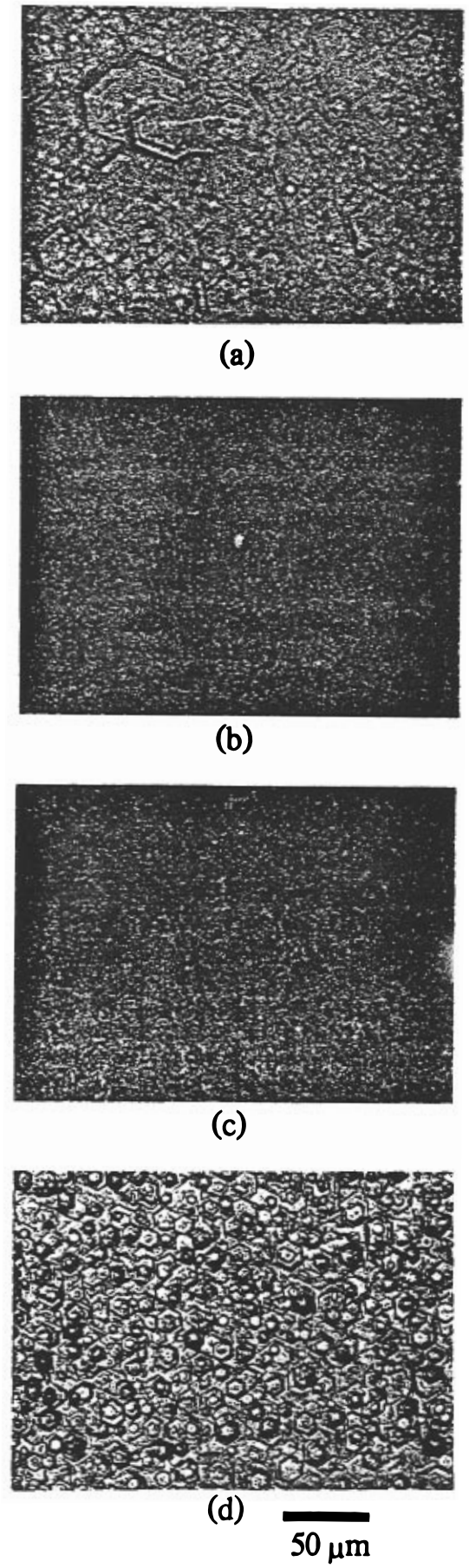

Figure 5. Interference micrographs of the surface of GaN films grown with and without a GaN buffer layer. The growth times of the buffer layers of each sample were (a) 30, (b) 70, (c) 70, and (d) 0 s. Reprinted with permission from ref 53. Copyright 1991 Japanese Journal of Applied Physics.

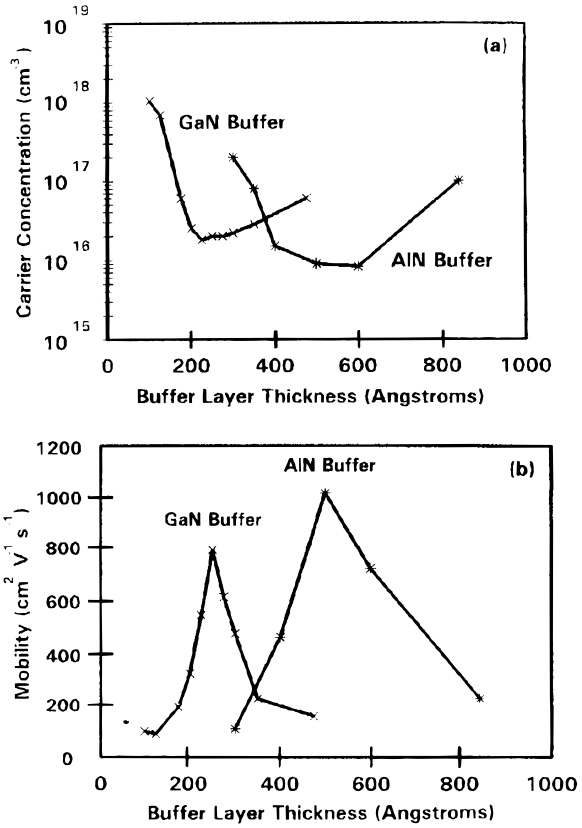

Figure 6. (a) Carrier concentrations and (b) electron mobilities of 4.0 mm GaN layers as a function of GaN and AlN buffer layer thickness on (0001) sapphire. Reprinted with permission from ref 60. Copyright 1993 American Institute of Physics.

growth of epilayers at higher temperatures 900−1100 °C.[52c−h,53] The AlN and GaN buffer layers are amorphous when deposited. During the heating step prior to growth of the epilayer, the buffer layer crystallizes by solid-phase epitaxy and forms columnar fine crystals with preferred orientation. Coalescence of the islands results in defect-free domains in the buffer layer with low-angle grain boundaries. The buffer layer is proposed to provide a significantly larger number of nucleation sites for the subsequent GaN growth, allowing pseudo two-dimensional growth to dominate, and concentrating defects at the interface.[59]

Crystal quality, surface morphology, electrical and optical properties have been shown to be critically dependent on the thickness and quality of the buffer layer (Figures 5 and 6).[60] The sensitivity of the epilayer to buffer layer growth conditions may be related to incorporation of various defects or impurities in the buffer layer during growth or to the surface morphology of the buffer layer surface. GaN film properties grown on *a*-plane sapphire have been reported to be much less sensitive to the buffer conditions than growth on *c*-plane sapphire which is tentatively attributed to a better surface polish and/or a better lattice mismatch.[61]

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Initial nitriding of the sapphire substrate is reported to improve the heteroepitaxial interface between AlN[62] and GaN[63] and sapphire than nonnitrided sapphire. Initial nitriding of sapphire before growth of the low-temperature buffer layer resulted in a buffer layer consisting of grains with only one orientation. In contrast, as discussed earlier GaN buffer layers deposited on sapphire contain grains of many random orientations. Improved electrical and optical properties are reported for GaN films grown on such prenitrided GaN buffer layers.[64] Sasaki has reported that the GaN(0001) surface is stabilized (necessary for smooth film morphology) on AlN buffered sapphire under the following growth conditions: high H_2 partial pressure, high total pressure, high growth temperatures, and low growth rate.[65]

As-grown GaN films are known to contain a high density of defects, due to the large lattice mismatch and thermal expansion coefficient difference between the epilayer and the substrate. Although two-step growth improves film crystallinity, the films still contain a large structural defect density of about 2×10^{10} cm^{-2} (Figure 7).[66] Despite the extremely high density of structural defects, highly efficient light-emitting diodes (LEDs) have been fabricated. The electronic properties of the more ionic materials such as GaN appears to be more tolerant of high defect densities than more covalent materials such as GaAs. In addition to the large lattice mismatches between the epitaxial layer and substrate, which can lead to high defect densities, heteroepitaxial growth encounters the problem of lattice distortion due to the presence of residual stress. The residual stress might arise from the large difference in lattice parameters or thermal expansion coefficients.[67] Wafer bending and cracking result during cooling from growth temperatures.[68] TEM analysis of GaN films grown by the two-step method reveal that the dominant defect in the GaN films are threading dislocations resulting from the misfit strain introduced by the lattice mismatch between the epilayer and the substrate, and low-angle grain boundaries, caused by small misorientations of GaN islands nucleated on the buffer layer during initial stages of growth. The nature of these threading dislocations suggests that careful optimization of the thickness and deposition temperature of the buffer layer is necessary to minimize or avoid formation of grain-type structures in the GaN film.[69]

Superior crystalline quality has been reported for GaN epilayer on GaN buffered sapphire by low-pressure chemical vapor deposition (LPCVD 60 Torr). A full width at half-maximum (fwhm) value of 37 arc sec was reported and TEM analysis revealed no stacking faults

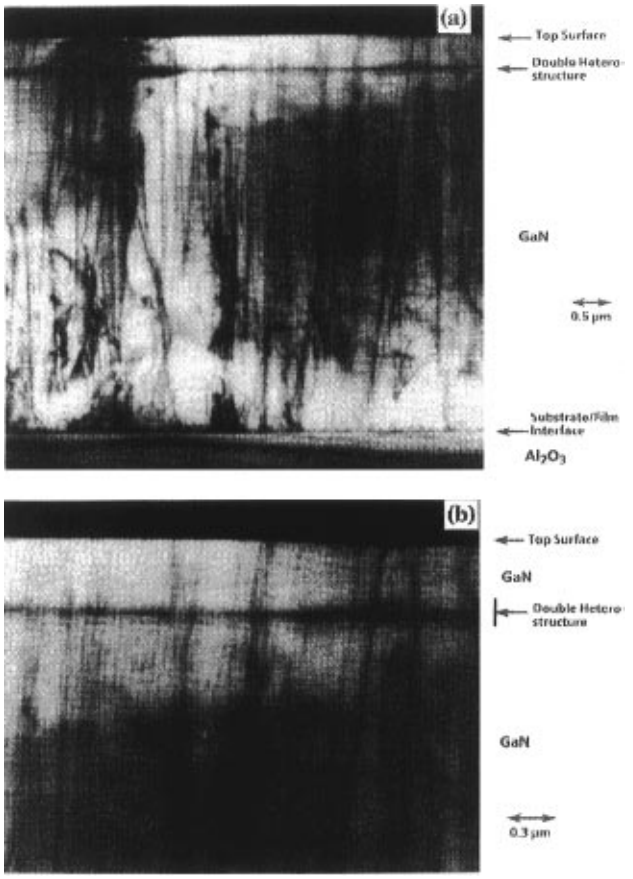

Figure 7. Bright-field two-beam TEM micrographs showing the defect distribution along a GaN blue light emitting diode from Nichia Chemical. (a) Cross section of full thickness of device; (b) top region of device including the double heterostructure active region. The dislocation density is in the range $(2-10) \times 10^{10}$ dislocations/cm^2. Reprinted with permission from ref 66a. Copyright 1995 American Institute of Physics.

or columnar growth.[70] The narrowest rocking curve fwhm value of 30 arc sec was reported for GaN grown by LPCVD (76 Torr) with an AlN buffer layer.[71] In contrast to atmospheric pressure chemical vapor deposition (APCVD), TEM analysis of GaN and AlN buffer layers grown by LPCVD (76 Torr) revealed a smooth surface morphology and a single crystalline nature.[72] The improved crystalline nature of the buffer layers grown by LPCVD may contribute to the superior crystalline quality of the GaN films grown by LPCVD described above.

Molecular Beam Epitaxy

MBE technology using reactive nitrogen sources is a favorable growth technique for group III nitrides because of the reduced growth temperature, growth of as-grown p-type layers, and high compositional controllability of monolayer thickness. Low-temperature growth has the potential of fabricating stoichiometric epitaxial layers at relatively low nitrogen supply ratios. Several

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types of reactive nitrogen sources, such as electron cyclotron resonance (ECR) microwave plasma,[73,83,84] microwave N_2 plasma,[74] ion source,[46] and RF (radio frequency) radical plasma source[75] have been coupled with MBE for the growth of group III nitrides. Because of the strong N−N bond in N_2 plasma assistance is necessary for excitation of the nitrogen molecule and generation of nitrogen atoms and radicals. However, plasma N_2 sources present a tradeoff between nitrogen supply and ion damage that is a byproduct of the source. The GaN growth rate is limited by the available flux of low kinetic energy reactive N species. This growth rate is quite small 0.4−0.04 μm/h. If higher growth rates are attempted, Ga droplets form on the surface due to insufficient nitrogen supply. Higher nitrogen fluxes are obtainable at higher plasma power but more energetic ions are created, which may degrade material quality by ion bombardment.[76] An increase in GaN lattice strain has been observed at higher input powers.[77] Reducing the relative concentration of ion to excited neutral (atomic and metastable molecular) nitrogen species results in a substantial improvement in the films' optoelectronic properties.[78] Promising results are being achieved using biasable substrates and adjustable grid voltages to eliminate the higher energy ions.[79] GaN films grown by ECR-MBE with a flow-limiting exit aperture on the ECR source were found to have superior structural, electrical and optical properties.[80] The low growth rates are a serious limitation of the plasma-enhanced MBE compared to MOCVD, which offers device-quality films at faster growth rates. More reactive nitrogen species such as ammonia,[81] dimethylhydrazine,[82] and hydrogen azide[83] have been investigated as the nitrogen source for MBE growth of group III nitrides.

As observed for films grown by MOCVD, higher quality films are grown on buffered substrates. For example, single-crystalline GaN (0001) has been grown by electron cyclotron resonance molecular beam epitaxy (ECR-MBE) on AlN buffered sapphire,[84] AlN buffered Si,[85] by reactive ion molecular beam epitaxy on AlN buffered sapphire,[86] and by reactive magnetron sputter deposition on AlN buffered GaAs.[87] Epitaxial (0001) AlN films have been grown by plasma-assisted gas source molecular beam epitaxy on a 6H-SiC,[88] and by rf diode sputtering on Si.[89] At lower substrate temperatures (275−350 °C) transparent, weakly oriented, polycrystalline GaN (0001) films were deposited on Corning 7059 glass with Ga and activated N_2 by ECR plasma-assisted deposition.[90]

Heteroepitaxial Growth of Zinc Blende Group III Nitrides.

Growth of zinc blende (cubic) group III nitrides has lagged behind growth of the thermodynamically favored wurzitic phase. The cubic-phase material may be superior for certain device applications and may be more readily integrated with existing high-quality III−V semiconductor substrates and devices. Most cubic group III nitrides have been grown by MBE on GaAs substrates. The crystal structure of epitaxial zinc blende GaN is strongly influenced by the substrate material and orientation. Zinc blende GaN has been epitaxially stabilized on β-SiC-coated Si(100),[91] MgO,[46] and 3C−SiC,[92] which are closely lattice matched, and on GaAs-(100),[93] nitrided GaAs(100) substrates,[94] and Si.[95] The cubic GaN phase is obtained by optimizing the param-

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eters that affect initial nucleation. Conditions such as predeposition annealing, nitridation of the substrate surface, buffer layers, and growth temperature are critical in determining the phase and crystallinity of the resulting layers. For example, zinc blende GaN on Si (001) substrates can be attained only if the GaN buffer is epitaxially grown on Si (001) in the zinc blende structure. If the GaN buffer is either amorphous or polycrystalline, the subsequent GaN film grows in the wurtzitic structure.[94] During MBE growth, the crystal structure of GaN was controlled by varying the incident arsenic overpressure. High-quality cubic GaN was grown at 700 °C with an arsenic overpressure with no evidence of GaAs incorporation.[96]

Nitridation of the GaAs (100) surface with hydrazine,[97] 1,1-dimethylhydrazine,[82] ammonia,[98] microwave-excited ammonia plasma,[99] activated N_2 from a cold cathode gun,[100] activated N_2 from an ECR generator,[101] and electron[102] and laser[103] irradiation of ammonia before growth has been found to promote epitaxial growth of cubic GaN.

A zinc blende InN polytype with a InAs interlayer (~80 nm) was grown on GaAs(100) substrates by plasma-enhanced molecular beam epitaxy. A TEM microstructural study revealed a high density of stacking fault defects from which wurtzite domains of InN were nucleated.[104]

Heteroepitaxial Growth of InN, InGaN, and InAlN

To realize the full potential of the group III nitride semiconductor system, the growth of each member must be optimized and alloys and superlattices using the alloys formed. The growth of InN is particularly important because it has the lowest energy bandgap (1.9 eV). By alloying InN into either AlN or GaN the bandgap of the semiconductor can be lowered into the 2−3 eV range, a critical range for making high-efficiency green and yellow visible light sources and detectors. Growth of high-quality InN films has proven difficult because of the low dissociation temperature (550 °C) of InN.[105] The nitrogen equilibrium vapor pressure over InN is orders of magnitude greater than over AlN or GaN. To combat this difficulty, low deposition temperatures (<600 °C) and various growth techniques such as reactive evaporation,[106] ion plating,[107] reactive radio-frequency (rf) sputtering,[108] reactive magnetron sputtering,[109] vapor phase epitaxy,[110] microwave-excited MOCVD,[111] laser-assisted CVD,[112] halogen transport,[113] and MBE[114] have been explored to obtain InN films.

Most InN growth has been conducted at ~500 °C. The best films are obtained with high indium and nitrogen fluxes. Short thermal anneals (30 min, 450−500 °C) have been shown to improve the crystallinity of the as-deposited InN films. InN films are generally polycrystalline with agglomerates of small columnar grains having varying degrees of texture and epitaxy. The crystalline improvement observed after annealing is attributed to rearrangement of these crystallites in the films. The electrical properties of the as-deposited InN films are dominated by connectivity between the grains.[115] Use of an AlN buffer layer on sapphire altered the granular polycrystalline growth mode of InN films resulting in substantial improvements in growth morphology and electrical properties. However, the electrical transport properties are still dominated by intergranular interactions.[116]

The ternary compound semiconductor InGaN, which has a direct band gap from 1.9 to 3.4 eV and the

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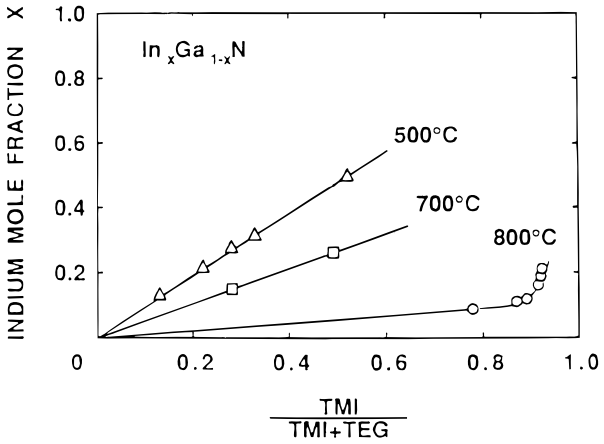

Figure 8. Incorporation of indium mole fraction in InGaN as a function of flow rate of indium to the sum of group III sources and growth temperature. Reprinted with permission from ref 121a. Copyright 1992 The Minerals, Metals & Materials Society.

quaternary InGaAlN system, which has a direct bandgap tunable from 1.9 to 6.2 eV, are promising materials for the active layer of double-heterostructure light-emitting diodes and laser diodes. However, incorporation of indium is difficult because of InN low dissociation temperature (~500 °C). A high nitrogen vapor pressure is required to prevent the dissociation of the In−N bond.[117] Poor-quality InN, InAlN, and InGaN films with a high indium mole fraction have been grown at low growth temperatures (~500−700 °C) with an activated nitrogen source by metal−organic molecular beam epitaxy (MOMBE[118]) or microwave-excited chemical vapor deposition.[119] At elevated growth temperatures (~800 °C), ternary alloy InAlN and InGaN films have been grown by atmospheric pressure MOCVD with improved crystallinity and optical and electrical properties. However, only low indium mole fractions, <33%, are incorporated at the higher growth temperatures, because the incorporation efficiency of indium decreases dramatically with increasing growth temperatures (Figure 8).[120] To combat the problem of InN dissociation high ammonia and indium fluxes are used. A trimethylindium flux as much as 12−20 times that of trimethylgallium is necessary leading to the consumption of several grams of trimethylindium per run.[121] High-quality InGaN was grown at 600−700 °C by ALE which minimizes gas-phase reactions with a significant reduction in indium precursor consumption.[122] The poor indium incorporation efficiency at higher growth temperatures may be related to (a) premature decomposition of the metalorganic precursor, (b) desorption of species involved in growth, and (c) adduct formation with ammonia, which may undergo premature reaction with methane elimination and consequently lower trimethylindium concentration. Similar difficulties incorporating indium and observation of parasitic reactions with AsH_3 and PH_3 have been reported in growth of InGaP and InGaAs alloys by MOCVD.[123]

An improvement in crystalline quality was observed for InGaN growth on the well matched ZnO substrate compared to growth on bare (0001)sapphire.[124] Deposition of high-quality AlGaN layers has been reported by MOCVD on self-nucleated sapphire[125] and on AlN buffered sapphire.[126]

Electrical Properties and Doping

Over a wide range of intentional and unintentional doping conditions, for various growth methods of group III nitrides, electron-transport measurements usually yield data which suggest strongly compensated material, with the degree of compensation independent of growth technique.[127] To date nearly all growth procedures have resulted in GaN layers with n-type conduction with large free electron concentration (10^{19}−10^{20} cm^{-3}) and low mobility (10−20 cm^2/V s). Even the best films have electron concentrations of 4×10^{16} cm^{-3}. Indium nitride films have electron concentrations in excess of 10^{18} cm^{-3}, whereas AlN is observed to be insulating, probably because its donor acceptor and defect levels lie deep within the bandgap. The nature of n-type autodoping phenomenon in GaN is still not understood. The n-type conductivity in unintentionally doped GaN layers has been attributed to nitrogen vacancies.[46,128] Alternate models attributing the n-type conductivity to some other intrinsic defect or residual impurity[129] have also been proposed. Oxygen incorporation (during growth)[130] and interface defects[131] have been shown to increase conductivity. Residual *n*-type conduction in GaN has been reported to result from a

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band of delocalized donors.[132] Recent studies suggest that n-type behavior is associated with intrinsic defects in the material.[133] However, the identity of the defect responsible for n-type conductivity in undoped group III nitrides is still in question.

As-deposited intentionally doped p-type GaN films, usually doped with Mg are compensated, highly resistive materials ($\rho \sim 10^4\ \Omega$ cm).[134] Recent studies suggest that compensation in p-type films occurs via intrinsic donor defects.[135] Low resistivity ($\rho < 2\ \Omega$ cm) p-typeGaN has been obtained after low-energy electron-beam irradiation (LEEBI)[116] or a N_2-ambient thermal anneal (500−700 °C).[136] The first report of p-type conduction in Mg-doped AlGaN was reported after annealing the as-deposited film at 1140 °C.[137] Hydrogen produced by dissociation of NH_3 on the surface of GaN is thought to passivate the p-type dopants through the formation of acceptor−H complexes, i.e., Mg−H complexes.[138] The Mg−H defect complexes are proposed to convert to conventional acceptor impurities by annealing or LEEBI.[139] Activation ratios of only 10^{-2}−10^{-3} are generally achieved, possibly due to the large binding energy of Mg and residual H contamination. Thus, to obtain high doping levels, large amounts of Mg must be incorporated.[1b] Hydrogenation of p-type GaN at 250 °C has been shown to passivate the acceptor dopants and to be reversible upon annealing.[140] GaN films with the highest hole mobilities (>400 cm^2/V s) and lowest carrier concentrations (5×10^{11} cm^{-3}) were grown in a hydrogen-free environment by reactive ion MBE.[141] Hydrogen and deuterium have been shown to have a high thermal stability in group III nitride films. Annealing temperatures greater than 800 °C are necessary to completely outdiffuse hydrogen and deuterium from GaN and AlN and temperatures > 600 °C for InN films.[142] Consequently, hydrogen in the growth ambient and subsequent processing steps[143] should be minimized to prevent passivation of the acceptor donors by hydrogen.

MOCVD Precursors for Growth of Group III Nitrides

This review will focus on MOCVD precursors used specifically for growth of group III nitrides.[144] Suitable MOCVD precursors should have sufficient volatility and stability to be transported to the surface and have the appropriate reactivity to decompose thermally into the desired solid and generate readily removed gaseous side products. Ideally, the precursors would be nonpyrophoric, water and oxygen insensitive, noncorrosive, and nontoxic. The commonly employed MOCVD precursors trimethylgallium, trimethylaluminum, or trimethylindium and ammonia used for the growth of the group III nitrides satisfy the first criteria of sufficient volatility and appropriate reactivity, but the trialkyl compounds are pyrophoric and extremely water and oxygen sensitive and ammonia is extremely corrosive. Other difficulties associated with the commonly employed precursors include the need for huge overpressures of ammonia (as great as 10^4) to minimize nitrogen dissociation from the growing film and to compensate for poor ammonia cracking efficiencies.[145] In addition predeposition reactions between trialkyl metal (trimethylgallium, trimethylaluminum, or trimethylindium) and ammonia are commonly encountered. The metal alkyls often form less volatile adducts with ammonia, making reliable transport difficult. Solutions to the aforementioned problems include modified reactor design with coaxial delivery tubes that keep the reactants separate until just before the substrate, low operating pressures, or alternative source materials that do not form adducts, are water and oxygen insensitive, and are nonpyrophoric.

Adduct formation with ammonia between trimethylaluminium or trimethylgallium is well documented. Adduct formation between trimethylgallium or triethylgallium and ammonia is complete in less than 0.2 s following mixing at room temperature. The resulting adduct, $Ga(CH_3)_3{\cdot}NH_3$ has a vapor pressure of 0.92 Torr at room temperature, while the vapor pressure of $Ga(C_2H_5)_3{\cdot}NH_3$ is much lower.[146] Thermal decomposition of the solid adduct $Ga(CH_3)_3{\cdot}NH_{3(s)}$ at 120 °C under 450 Torr of nitrogen results in the evolution of methane and the formation of the trimer $[(CH_3)_2GaNH_2]_3$, which was characterized by single-crystal

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analysis (Figure 9):[147]

$$3Ga(CH_3)_3{\cdot}NH_{3(s)} \rightarrow [(CH_3)_2GaNH_2]_3(s) + 3CH_4(g) \quad (1)$$

The corresponding aluminum adduct $Al(CH_3)_3{\cdot}NH_3(s)$ decomposes in a few days at room temperature with evolution of methane to form the trimer $[(CH_3)_2AlNH_2]_3(s)$, which is structurally similar to $[(CH_3)_2GaNH_2]_3$.[148] In the gas phase, a trimer−dimer−monomer equilibria is observed. Decomposition of $[(CH_3)_2AlNH_2]_3$ begins at 125 °C with evolution of methane.[149] In solution, the decomposition mechanism of $(CH_3)_2Al{\cdot}NH_3$ was found to be autocatalytic.[150] Amine-catalyzed ring opening was observed with addition of ammonia and methylamine to $[(CH_3)_2AlNH_2]_3$. The ability of amines to open AlN rings suggests an explanation for empirical observations that pyrolysis of R_2AlNH_2 ($R = CH_3$, C_2H_5) amides under ammonia yields AlN of improved purity and crystallinity.[151] Ring opening by ammonia would facilitate skeletal rearrangement and RH elimination over pyrolysis of the alkyl groups.[152]

During chemical vapor deposition of group III nitride films with R_3M ($R = CH_3$, C_2H_5, M = Al, Ga, In) and ammonia successive displacement reactions of the alkyl by ammonia is believed to result in the formation of the nitride film as illustrated below for the growth of AlN from trimethylaluminum and ammonia (eqs 2−5).[153] Similar reactions would be expected for the formation and GaN from trimethylgallium and ammonia[154] and InN from trimethylindium and ammonia.

$$(CH_3)_3Al + NH_3 \rightarrow (CH_3)_3Al{\cdot}NH_3 \quad \text{ammonia adduct} \quad (2)$$

$$(CH_3)_3Al{\cdot}NH_3 \rightarrow CH_4 + [(CH_3)_2AlNH_2]_n \quad \text{amide} \quad (3)$$

$$[(CH_3)_2AlNH_2]_n \xrightarrow{\Delta} CH_4 + [CH_3AlNH]_n \quad \text{imide} \quad (4)$$

The surface chemistry of aluminum nitride formation on alumina using trimethylaluminum and ammonia as precursors has been studied in detail. The coadsorption of ammonia and trimethylaluminum on alumina surface

$$[CH_3AlNH]_n \xrightarrow{\Delta} CH_4 + AlN \quad \text{nitride} \quad (5)$$

results in a surface adduct, ammonia, and bridge-bonded NH_2. The adduct structure is proposed to be $(CH_3)_2Al{\cdot}NH_3$ with Al bonded to surface oxygen and hydrogen. Evidence of hydrogen bonding between surface oxygen and hydrogen in NH_3 is observed for some of the adduct species and excess NH_3. The minimum temperature of AlN formation was observed to be 330 °C. Additional heating of the surface generates more AlN, AlNN, and HAlNN species on the surface. At 777 °C the only species observed on the surface are AlN and AlNN. Bridge-bonded 4-coordinate NH_2 was proposed to lead to AlN and 3-coordinate NH_2 to result in AlNN, dinitrogen complexes.[155]

Several alternative group III alkyl MOCVD sources have been investigated to produce aluminum-, gallium-, and indium-containing films, including triethyl and triisopropyl. These sources all pyrolyze below 250 °C. Carbon levels in the resultant thin films are greatly reduced relative to films grown with trimethyl derivatives. Carbon reduction is attribution to a more efficient β-hydride elimination decomposition pathway.[156] Use of a trialkyl group III precursor other than trimethyl may result in improved film quality, lower oxygen and carbon incorporation, and/or lower deposition temperatures. In fact, GaN with one of the narrowest fwhm of 37 arc sec was grown with triethylgallium.[70]

Coordinatively saturated precursors, such as trimethylindium−trimethylamine adduct $(CH_3)_3In{\cdot}N(CH_3)_3$,[157] trimethylindium−diisopropylamine adduct $(CH_3)_3In{\cdot}NH(CH(CH_3)_2)_2$,[158] or dimethylamidodiethylindium $(C_2H_5)_2InN(CH_3)_2$,[159] or an intramolecular adduct, such as 1,3-[(dimethylamino)propyl]dimethylindium $(CH_3)_2N(CH_2)_3In(CH_3)_2$ (Figure 10a)[160] are attractive because they are nonpyrophoric, relatively insensitive to oxygen and water, and less likely to form adducts than the trialkyl precursors. Growth of high-quality low-oxygen III−V materials has been demonstrated with the coordinatively saturated 1,3-[(dimethylamino)-propyl]-1-gallacyclohexane (Figure 10b)[161] and 1,3-[(dimethylamino)propyl]-1-alacyclohexane (Figure 10c)[162] precursors. Use of the coordinatively saturated compounds may be restricted to low-pressure growth tech-

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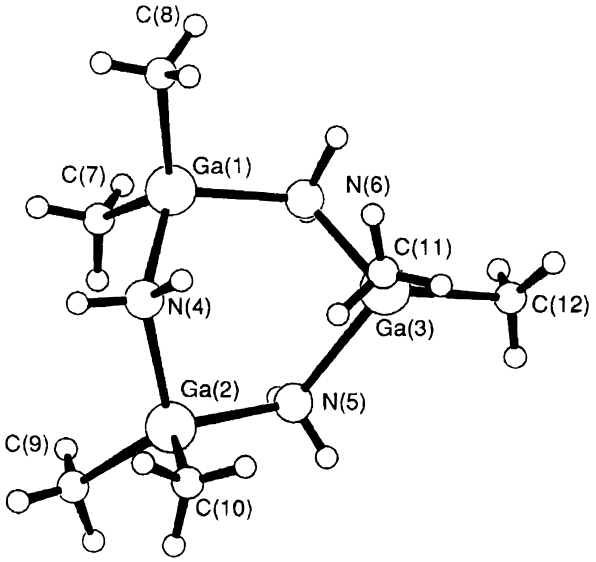

Figure 9. Molecular structure of $[(CH_3)_2GaNH_2]_3$. Reprinted with permission from ref 147a. Copyright 1992 The Royal Society of Chemistry.

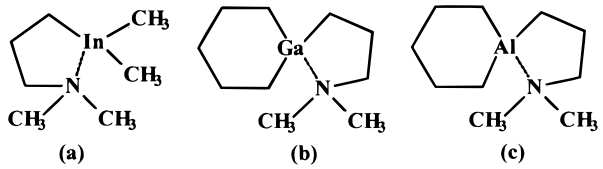

Figure 10. Chemical structure of (a) [(dimethylamino)propyl]-dimethylindium, (b) 1,3-[(dimethylamino)propyl]-1-gallacyclohexane, and (c) 1,3-[(dimethylamino)propyl]-1-alacyclohexane.

niques because of their relatively low vapor pressures as compared to the commonly employed trialkyl precursors.

Use of trimethylamine alane, $(CH_3)_3N{\cdot}AlH_3$ is known to dramatically reduce carbon and oxygen levels in AlGaAs.[163] However, the extreme reactivity of the hydride derivatives, such as trimethylamine alane and gallane,[164] limit their usefulness for MOCVD growth of group III nitride films. Trimethylamine alane and ammonia are known to react in the gas phase at room temperature, liberating trimethylamine and hydrogen and forming $(HNAlH)_n$, a polymeric material.[165] The trimethylamine alane and ammonia reaction on an alumina surface is similar to the gas-phase reaction.[166] Trimethylamine gallane, $(CH_3)_3N{\cdot}GaH_3$, is substantially less stable than trimethylamine alane[167] and has been shown to react with ammonia at room temperature to form cyclotrigallazane, $[H_2GaNH_2]_3$, which can be further pyrolized to give cubic GaN powder.[168] Trimethylamine alane is best suited for low-pressure processes such as MOMBE[169] or ALE[170] which minimize parasitic gas-phase reactions.

The most commonly employed nitrogen source is ammonia. However, ammonia is extremely corrosive and does not readily decompose at temperatures below 800 °C.[171] Although dissociation of ammonia has been observed at lower temperatures on silicon surfaces[172] and group III nitride films have been grown at temperatures <800 °C by a variety of techniques, substrate temperatures in excess of 800 °C are routinely employed to grow epitaxial device-quality group III nitride films with ammonia. High growth temperatures are known to introduce thermal stresses in the films, enhance impurity diffusion, and hinder indium incorporation. To compensate for poor ammonia cracking efficiencies and to minimize nitrogen dissociation from the growing film, huge overpressures of ammonia are employed. Another difficulty with ammonia is the formation of less volatile adducts with the group III alkyl precursors such as trimethylgallium, trimethylaluminum, or trimethylindium making reliable transport difficult. Thus, alternative nitrogen sources such as NF_3, hydrazine (N_2H_4), 1,1-dimethylhydrazine ($(CH_3)_2NNH_2$), hydrogen azide (HN_3), *tert*-butylamine (^{t}BuNH$_2$), and isopropylamine (^{i}PrNH$_2$) have been explored.

Alkylamines such as *tert*-butylamine have been considered as ammonia replacements. Growth of AlN by plasma-excited MOMBE at temperatures <700 °C could not be obtained with *tert*-butylamine as the nitrogen source, due to the poor decomposition efficiency of *tert*-butylamine at low temperatures. Growth of AlN was observed at higher temperatures, but the films were of poor crystallinity and wet-etched substantially faster than ECR-plasma derived AlN.[173] High carbon levels (14−17 atom %) were observed in AlN films grown using trimethylaluminum and isopropylamine gas mixtures.[134] Slightly lower carbon levels (3−9 atom %) were observed in AlN films grown using *tert*-butylamine and trimethylaluminum or ^{t}Bu$_3$Al gas mixtures.[174] Directly bonded species such as $((CH_3)_2AlNHR)_2$ R = ^{t}BuNH$_2$ and ^{i}PrNH$_2$ were proposed to form in situ in the gas phase prior to film growth. In conclusion, alkylamines are poor nitrogen sources for the growth of nitrides due

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to their poor decomposition efficiency which is directly related to the strength of the C−N bond.

Trifluroamine (NF_3) was considered as a potential ammonia alternative because it has a relatively weak N−F bond (60 kcal/mol) and is not known to form adducts. In contrast, ammonia has strong N−H bonds (110 kcal/mol)[175] and acts as a strong Lewis base to form adducts with Lewis acid acceptor molecules such as trimethylgallium or trimethylaluminum. No gas-phase reactions were observed between ammonia and trimethylaluminum, trimethylgallium, or triethylgallium and NF_3.[176] However, when trimethylaluminum and NH_3 were reacted at 58 °C in the gas phase, $(CH_3)_2AlF$ was observed and may be a route for incorporation of AlF_3 impurities in AlN.[177] Polycrystalline AlN films grown with trimethylaluminum and NF_3 at ∼500 °C by MOCVD were observed to be contaminated with AlF_3.[178] Therefore, NF_3 is not a good nitrogen source.

Hydrazine (N_2H_4) and 1,1-dimethylhydrazine have been proposed as alternatives to ammonia for lower temperature growth, because dissociation of the NH_2−NH_2 bond (71 kcal/mol)[179] can occur more readily than loss of H from ammonia (110 kcal/mol). However, hydrazine and 1,1-dimethylhydrazine are toxic and flammable. Care must be taken in the handling and storage of hydrazine to exclude oxidants and metals which can explosively decompose hydrazine.[180] Hydrazine has been reported to form a bis adduct with trimethylgallium or trimethylaluminum in the gas phase (eq 6). The adduct is believed to decompose with

$$2(CH_3)_3Ga + N_2H_4 \rightarrow (CH_3)_3GaNH_2H_2NGa(CH_3)_3 \quad (6)$$

$$(CH_3)_3GaNH_2H_2NGa(CH_3)_3 \rightarrow (CH_3)_2GaNHHNGa(CH_3)_2 + 2CH_4 \quad (7)$$

loss of methane to form the amide (eq 7) at temperatures < 100 °C. Growth of GaN was achieved through the pyrolysis of the bis adduct. Good-quality GaN was obtained at 900 °C growth temperature with Hall mobilities of 50 cm^2/Vs and carrier concentrations of 6×10^{17} cm^{-3}.[181] In addition, a much lower hydrazine partial pressure is needed for the growth of GaN films than ammonia.[182] Hydrazine is a good nitrogen source, but its toxic and explosive nature limits its usefulness.

Dimethylhydrazine has been used as a nitrogen source in gas source MBE (GSMBE) to nitride GaAs surfaces and for growth of GaN on GaAs. However, the obtained GaN epilayers contain a lot of carbon impurities and have poor crystalline properties.[82] Surface studies of the thermal nitridation of GaAs(100) with 1,1-dimethylhydrazine indicate that dimethylhydrazine dissociates with cleavage of the N−N bond during adsorption above 127 °C on GaAs (100).[183] The decomposition pathway of dissociated dimethylhydrazine on the surface may be similar to that of the alkylamines, leading to large carbon incorporation.

Another alternative nitrogen source which has been considered is hydrogen azide (HN_3). Hydrogen azide has a high vapor pressure (bp 37 °C) and is a highly reactive, easily thermally decomposed molecule. Hydrogen azide decomposes at ∼300 °C to form an N_2 molecule and a metastable HN (nitrene) radical with two dangling bonds which provides a ready source of active nitrogen. However, hydrogen azide is highly toxic and in the liquid state at high pressures is potentially explosive. Surface studies indicate that GaAs (110) and (100) substrate surfaces could be nitridated by photodissociation of HN_3 with 308 nm excimer laser radiation.[184] Preliminary film growth results with trimethylgallium and hydrogen azide at 600 °C, 10^{-6} mbar resulted in flat, uniform, highly oriented polycrystalline GaN films.[185] Polycrystalline InN films have been grown by laser-assisted chemical vapor deposition with trimethylindium and HN_3 on Si(100) at 427 °C under low-pressure conditions.[186] Epitaxial GaN was grown with triethylgallium and HN_3 under similar conditions.[187] GaN films grown with hydrogen azide by MBE were smoother, more uniform, with no surface damage, and had greater growth rates than GaN films grown with an ECR plasma.[83] Hydrogen azide is a good nitrogen source for nitride growth but suffers from its toxic and potentially explosive nature.

Alternative source materials that contain both the group III and the nitrogen delivering moiety in the same molecule have also been considered for the growth of group III nitrides. Polycrystalline GaN films were grown with triethylgallium monamine $\{(C_2H_5)_3Ga{\cdot}NH_3\}$ without an additional nitrogen source. However, $Ga(C_2H_5)_3{\cdot}NH_3$ decomposed in the saturator to form the diethylgallium amide $(C_2H_5)_2GaNH_2$, which underwent further decomposition and resulted in a noticeable decrease in vapor pressure and deposition rate of GaN films.[188] Although polycrystalline AlN films were grown by MOCVD with $[(CH_3)_2AlNH_2]_3$ at 500 °C,[189] Interrante has noted that on melting, $[(CH_3)_2AlNH_2]_3$ gradually converts to an insoluble, involatile solid of approximate composition $[CH_3AlNH]_n$. A similar reaction may be occurring during the decomposition of $(C_2H_5)_2GaNH_2$.

Alkylamine adducts and alkylamides of gallium[190] and aluminum have also been considered as precursors for GaN and AlN growth. As illustrated for tri-

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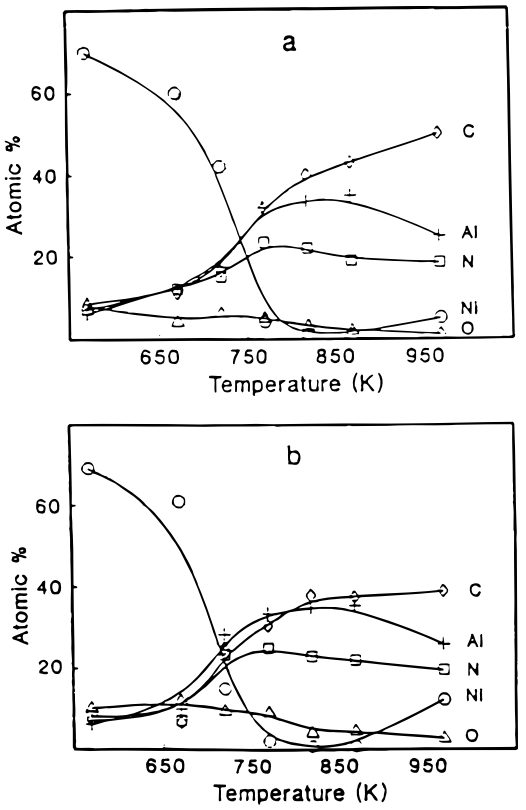

Figure 11. Atomic concentrations as determined by X-ray photoelectron spectroscopy of AlN films deposited on Ni (100) by the single-source precursors (a) $[(CH_3)_2AlNH^iPr]_2$ and (b) $[(CH_3)_2AlNH^tBu]_2$. Reprinted with permission from ref 193. Copyright 1994 The Korean Chemical Society.

methylaluminum and *tert*-butylamine, the alkylamine adducts are known to thermally decompose by amide formation and loss of methane from aluminum (eq 9).

$$(CH_3)_3Al + {}^tBuNH_2 \rightarrow (CH_3)_3Al{\cdot}NH_2{}^tBu \quad \text{amine adduct} \quad (8)$$

$$(CH_3)_3Al{\cdot}NH_2{}^tBu \rightarrow CH_4 + [(CH_3)_2AlN_4{}^tBu]_2 \quad \text{amide} \quad (9)$$

AlN films grown with the amides $[HAl(NR_2)_3]_2$ and $[HAl(NR_2)_2]_2$ {R = CH_3, C_2H_5} had atomic ratios of $AlC_{1.3}N_{0.05}O_{0.4}$ (surface) and $AlC_{1.2}N_{0.4-0.6}O_{0.06-0.2}$ (after argon sputter-etching 300−500 Å) as determined by Auger electron spectroscopy.[191] High carbon levels (15−38 atom %) and relatively more Al than N were observed in AlN films grown with $[(CH_3)_2AlN(CH_3)_2]_2$, $[(CH_3)_2Al(Azir)]_3$ {Azir = aziridine, NCH_2CH_2}, and $[(C_2H_5)_2AlNH^tBu]_2$ on Si(100) substrates.[192] AlN films grown on Ni(100) with $[(CH_3)_2AlNHR]_2$ (R = isopropyl, *tert*-butyl) also contained relatively large amounts of aluminum and carbon compared to nitrogen, and the carbon concentration was found to increase with temperature (Figure 11). Excess carbon was reported to result from methyl groups originally bonded to aluminum.[193] These results suggest that alkylamine adducts and group III alkylamides that contain C−N bonds are poor single sources for nitride growth.

Potentially better results may be observed by transammination or replacement reactions of the aluminum and gallium alkylamides with ammonia. Transammination of $Ga_2\{N(CH_3)_2\}_6$, hexakis(dimethylamido)digallium, at 200 °C with ammonia resulted in polycrystalline GaN films with carbon contents less than 2%. The key step might be the facile ammonia/dialkylamide transamination reaction where dimethylamine is replaced by ammonia (eq 10).[194] Dialkylamido complexes

$$Ga{-}N(CH_3)_2 + NH_3 \rightarrow Ga{-}NH_2 + HN(CH_3)_2 \quad (10)$$

and ammonia have been demonstrated to be excellent precursors for the deposition of other metal nitride films. For example nearly stoichiometric TiN films have been grown from tetrakis(dimethylamido)titanium and ammonia at temperatures of 200−400 °C.[195] The advantage of transammination with alkylamido gallium and aluminum complexes is the removal of all metal−carbon bonds, which should lead to a more facile decomposition mechanism and reduced carbon incorporation. The disadvantage is the lower volatility of the alkylamido complexes relative to alkyl species. For example, hexakis(dimethylamido)digallium sublimes at 70−80 °C under 10^{-2} Torr vacuum compared to trimethylgallium, which has a vapor pressure of ~1 Torr at room temperature.

A single-source precursor that incorporated a hydrazine substituent as the nitrogen-delivering substituent was used to grow GaN films. The films grown with dimethylhydrizodimethylgallium, $(CH_3)_2GaNHN(CH_3)_2$ were polycrystalline and had a poor surface morphology. Pyrolysis studies indicate that $(CH_3)_2GaNHN(CH_3)_2$ decomposes by cleavage of the Ga−N bond at 260 °C and the Ga−C bond cleaves around 500 °C. The poor film quality may be related to loss of the hydrazine nitrogen delivering ligand because of the facile cleavage of the Ga−N bond at 260 °C.[196]

A more promising nitogen-delivering species is an azide (N_3) substituent. Growth studies with the dialkylaluminum azides $[R_2AlN_3]_3$ (R = CH_3, C_2H_5)[197] and diethylgallium azide[198] resulted in nearly stoichiometric

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AlN and GaN films with carbon concentrations of ~10%. The amorphous AlN and GaN films were deposited on a variety of substrates at temperatures as low as 400 °C. Addition of ammonia during growth of GaN with diethylgallium azide improved film quality. Oriented GaN films were obtained at substrate temperatures >650 °C on (0001) sapphire with electron mobility of 45−50 cm^2/Vs and carrier concentrations of 2×10^{18} cm^{-3}.[199] Under chemical beam epitaxy conditions (pressure = 10^{-5}−10^{-4} Torr) polycrystalline GaN films were grown with dimethylgallium azide, $(CH_3)_2GaN_3$[200] at substrate temperatures 450−650 °C. Interestingly, highly oriented (0001) GaN was grown on a variety of substrates including (100) GaAs, (111) GaAs, (0001) sapphire and quartz. Slightly better quality GaN films were grown with dimethylgallium azide and dimethylhydrazine.[155]

Thin films of AlN were deposited by atmospheric pressure chemical vapor deposition (APCVD) with triethylaluminum and trimethylsilylazide $(CH_3)_3SiN_3$ at 300−450 °C. A growth mechanism involving the in situ formation of an intermediate gas-phase species such as dimethylaluminum azide, $(CH_3)_2AlN_3$, was proposed (eq 11).[201] The as-deposited films were nearly stoichiometric

$$(CH_3)_3SiN_3 + (CH_3)_3Al \rightarrow (CH_3)_2AlN_3 + (CH_3)_4Si \quad (11)$$

and had carbon concentration of 9%, similar to films deposited with the dialkylaluminum and gallium azides.

The most promising alternative single-source precursor to date is bis(dimethylamido)gallium azide, $((CH_3)_2N)_2GaN_3$, which combines labile amido ligands and an azide nitrogen delivering substituent. Bis(dimethylamido)gallium azide is a polymeric chain of dimers (Figure 12) with the azide substituent bridging two gallium centers and consequently has a lower vapor pressure than trimethylgallium or dimethylgallium azide. The more labile amido ligands compared to alkyl substituents results in a reduction in carbon incorporation in the subsequent GaN films and reduces growth temperature. For example, an amorphous GaN film with a 3.4 eV bandgap was deposited on (0001) sapphire at 250 °C with bis(dimethylamido)gallium azide. At a higher substrate temperature of 580 °C an epitaxial wurzitic (0001) 0.7 mm GaN film with a bandgap of 3.2 eV was deposited on (0001) sapphire in 3 h (Figure 13). Epitaxy was confirmed by a χ scan and partial pole figure analysis. Using GaAs implanted standards SIMS (secondary ion mass spectroscopy) analysis of the epitaxial film grown at 580 °C revealed a carbon content of 2×10^{21} atoms/cm^3. In contrast, the carbon levels in GaN films grown from dimethylgallium azide were too high to be measured by SIMS.[202]

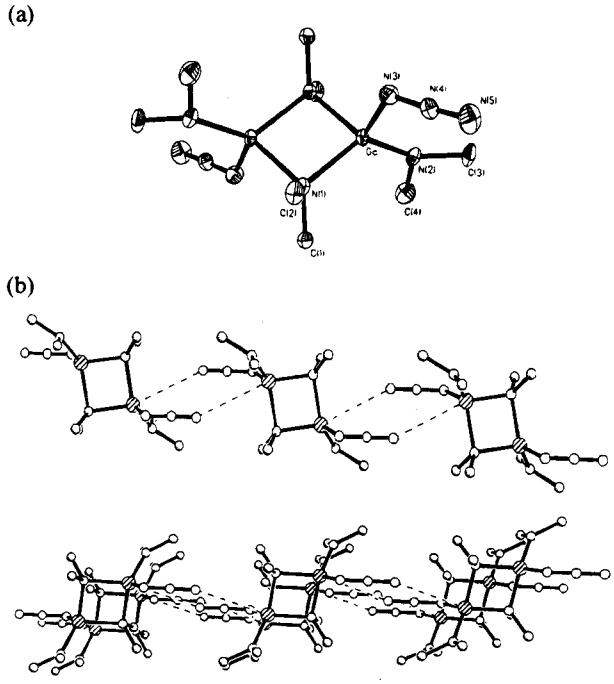

Figure 12. Molecular structure of bis(dimethylamido)gallium azide, $[(Me_2N)_2GaN_3]_2$. Thermal ellipsoid view of the dimer (a) is illustrated above. Selected bond distances (Å) and bond angles (deg) are as follows: Ga−N1 1.992(3), Ga−N1′ 1.998(3), Ga−N2 1.834(3), Ga−N3 1.919(4), Ga−Ga′ 2.8814(7), N1−C1 1.476(5), N1−C2 1.484(4), N1−Ga1′ 1.998(3), N2−C3 1.460(5), N2−C4 1.426(7), N3−N4 1.177(5), N4−N5 1.138(5); N2−Ga−N3 114.7(2), N2−Ga−N1 124.51(14), N3−Ga−N1 107.70(14), N2−Ga−N1′ 114.19(12), N3−Ga−N1′ 103.50(14), N1−Ga−N1′ 87.52, Ga−N1−Ga′ 92.48(11), N4−N3−Ga 124.8(3), N5−N4−N3 175.6(5). The polymeric chain (b) with hydrogen atoms omitted for clarity is illustrated below. Reprinted with permission from ref 202a. Copyright 1995 The American Chemical Society.

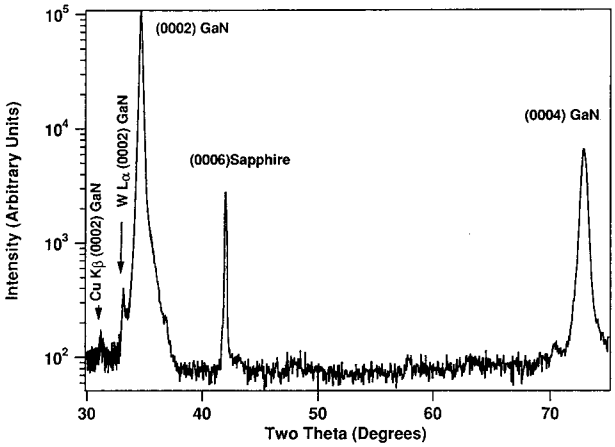

Figure 13. X-ray diffraction θ−2θ scan of a GaN film grown on (0001) sapphire with the single-source precursor, bis(dimethylamido)gallium azide, at a substrate temperature of 580 °C. Reprinted with permission from ref 202a. Copyright 1995 The American Chemical Society.

More reactive precursors, such as trimethylamine alane, hydrazine, hydrogen azide, or single-source precursors such as bis(dimethylamido)gallium azide which incorporate a facile decomposition pathway and a nitrogen-delivering substituent should be utilized in growth of group III nitrides by MOMBE (or GSMBE).

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MOMBE operates at near UHV conditions, facilitating the use of less volatile precursors and eliminating gas phase collisions thus limiting potential parasitic reactions between incompatible precursors. MOMBE reactions tend to be unimolecular and thermodynamically driven, and consequently film growth by MOMBE would benefit from the use of more reactive precursors. In contrast growth of group III nitrides by conventional MOCVD is driven by macroscopic, multiple molecule, complex reaction pathways. Incorporation of nitrogen in the growing nitride film is abetted by the use of huge overpressures of ammonia. Plasma activation of ammonia may enhance nitrogen incorporation. The use of more reactive trialkyl precursors such as triethylgallium may reduce carbon incorporation and improve film quality. Transamination with amido substituted group III precursors should be more thoroughly explored. Perhaps the biggest difficulty with conventional MOCVD growth is incorporation of indium at elevated growth temperatures. Use of a coordinatively saturated indium precursor may improve indium incorporation efficiencies by improving the thermal stability of the precursor during transport to the surface and minimizing parasitic reactions with ammonia.

Summary

The group III nitrides are primary candidates for applications in short-wavelength emitters and detectors and high-temperature, high-power electronics. However, high growth temperatures may limit compatibility and incorporation of group III nitrides with existing fabrication technologies and devices. The relation between deposition temperature and crystalline quality is not well understood. Several approaches are under consideration to lower deposition temperatures including various techniques to activate nitrogen. The potential of alternative precursors for MOCVD has been demonstrated, but device-quality films have yet to be grown with alternative precursors. The most pressing need is for an InN precursor which deposits high-quality InN at growth temperatures less than 500 °C and allows higher indium mole fractions to be incorporated in device quality ternary and quaternary alloys with gallium and aluminum nitrides.

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