Synthesis and Structure of a Novel Lewis Acid−Base Adduct, $(H_3C)_3SiN_3 \cdot GaCl_3$, en Route to Cl_2GaN_3 and Its Derivatives: Inorganic Precursors to Heteroepitaxial GaN

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The formation of a novel Lewis acid−base complex between the silyl azide $Si(CH_3)_3N_3$ and $GaCl_3$ having the formula $(H_3C)_3SiN_3 \cdot GaCl_3$ **(1)** is demonstrated. The X-ray crystal structure of **1** shows that the electron-donating site is the nitrogen atom directly bonded to the organometallic group. Compound **1** crystallizes in the orthorhombic space group *Pnma*, with cell dimensions $a = 15.823(10)$ Å, $b = 10.010(5)$ Å, $c = 7.403(3)$ Å, and $Z = 4$. Low-temperature decomposition of **1** via loss of $(H_3C)_3SiCl$ yields Cl_2GaN_3 **(2)**, which serves as the first totally inorganic (C,H-free) precursor to heteroepitaxial GaN by ultrahigh-vacuum chemical vapor deposition. A volatile monomeric Lewis acid−base adduct of **2** with trimethylamine, $Cl_2GaN_3 \cdot N(CH_3)_3$ (**3**), has also been prepared and utilized to grow high-quality GaN on Si and basal plane sapphire substrates. The valence bond model is used to analyze bond lengths in organometallic azides and related adducts.

Introduction

The potential microelectronic and optoelectronic applications of the wide-bandgap nitride semiconductors InN, AlN, and GaN have prompted considerable research into their growth and development. Gallium nitride, the most studied of the group III nitrides, has a bandgap of 3.4 eV and forms solid solutions with InN and AlN from which heterostructures can be fabricated.[1] GaN-based heterostructures and quantum-well light-emitting diodes have been developed and are commercially available. Recently, Nakamura and co-workers successfully demonstrated an InGaN-based multiquantum-well laser diode operating at 410 nm, the shortest wavelength ever generated by a semiconductor laser.[2] This achievement is widely recognized as a critical step toward realization of blue lasers for commercial applications such as optical storage. For applications in microelectronics, the strong bonding, high thermal stability, and wide bandgaps render the group III nitrides useful in high-power, high-temperature, and high-frequency devices.[3] Electronic devices ranging from field effect transistors to photodetectors have been demonstrated.[4] The further development and optimization of these microelectronic and optoelectronic devices require improved nitride material because, despite the many advances, serious problems still hinder the synthesis of high-quality thin films. These problems include a large background n-type carrier concentration due to nitrogen deficiencies, lack of suitable substrates, crystalline imperfections, and difficulties in p-doping.[5,6] Avoidance of a large concentration of nitrogen vacancies forces the use of low-temperature depositions; these now lead to the introduction of point, line, and planar defects that are likely to be electrically active.

Alternative synthetic routes to stoichiometric gallium nitride materials involve use of unimolecular (single-source) precursors containing strong Ga−N bonds. Particularly promising are precursors that contain the azide (N_3) ligand as the nitrogen source. Organometallic gallium azides, such as $(R_2GaN_3)_3$ (R = CH_3, C_2H_5) and $[(CH_3)_2N]_2GaN_3$ have been used to deposit stoichiometric GaN of reasonable crystal quality and chemical purity.[7−9] Most recently, thermal decomposition of a bis(azide) compound, $(N_3)_2Ga[(CH_2)_3N(CH_3)_2]$, on (0001) sapphire provided highly textured GaN films at 750 °C that however appeared to contain significant levels of impurities.[10] These methods permitted deposition at substantially lower temperatures than those required for traditional metal−organic chemical vapor deposition (MOCVD) processes which normally utilize reactions of $(CH_3)_3Ga$ or $(C_2H_5)_3Ga$ with large excesses of ammonia. They also have the potential of providing better deposition control at low pressures (since the precursors are not very volatile) as well as eliminating the inefficient use of ammonia, thus leading to more effective and economical deposition processes.

A major obstacle to the realization of device-quality nitride material is the difficulty of achieving p-type doping when growth techniques such as MOCVD are used. It has been determined that hydrogen impurities introduced during MOCVD growth at concentrations similar to those of the Mg acceptors form

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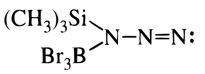
complexes with the dopant that severely diminish the doping efficiency of the MOCVD-grown material.[11] Our approach to GaN synthesis involves development of simple inorganic precursors that would allow growth in a carbon- and hydrogen-free deposition environment, that are compatible with p-doping processes, and that eliminate the possibility of carbon contamination in the films. We have succeeded in depositing heteroepitaxial GaN at very low pressures in an ultrahigh-vacuum chemical vapor deposition (UHV-CVD) chamber using, for the first time, an exclusively inorganic single-source precursor.[16] The new precursor compound, azidodichlorogallane (Cl_2GaN_3), is obtained from a convenient synthetic route involving the reaction of gallium trichloride with trimethylsilyl azide to yield a novel monomeric adduct of composition $(H_3C)_3SiN_3{\cdot}GaCl_3$ (**1**). Thermal decomposition of the adduct at slightly above its melting point (50 °C) quantitatively yields azidodichlorogallane (Cl_2GaN_3, **2**) by loss of $(H_3C)_3SiCl$. Moreover, interactions of Cl_2GaN_3 with trialkylamines result in monomeric adducts of the form $Cl_2GaN_3{\cdot}NR_3$ ($R = CH_3$, C_2H_5). The trimethylamine adduct, $Cl_2GaN_3{\cdot}N(CH_3)_3$, is not C−H free but is nevertheless a good low-temperature source of high-quality GaN. In this article, we report the synthesis and characterization (including an analysis of bond lengths) of these azide compounds as well as deposition and characterization of high-quality epitaxial GaN by use of UHV-CVD.

Results and Discussion

1. Synthesis of $(H_3C)_3SiN_3{\cdot}GaCl_3$ (1) and Bond Valence Analysis of Azides. In 1965, Thayer and West reported the existence of stable 1:1 adducts of the Lewis acids $SnCl_4$ and BBr_3 with organometallic azides of Si, Ge, and Sn.[12] Infrared studies of these complexes revealed that the azide band positions were substantially different from those of free azides and possibly corresponded to a bridging azide. On the basis of these IR data, a molecular structure was proposed in which the nitrogen bonded to the silicon (α-nitrogen) is the electron-donating site, shown as follows for the $(H_3C)_3SiN_3{\cdot}BBr_3$ compound (for comments on the bond order of the N−N bonds see below).



$$\begin{matrix}(CH_3)_3Si\diagdown & \\ & N{-}N{=}N{:} \\ Br_3B\diagup & \end{matrix}$$

Attempts to isolate analogous azide complexes of aluminum halides were not successful. In particular, reactions between $AlCl_3$ and $(H_3C)_3SiN_3$ resulted in formation of $AlCl_2N_3$ polymeric solids rather than molecular systems.[13] We found, however, that similar reactions of $GaCl_3$ lead to formation of the novel adduct $(H_3C)_3Si{-}N{-}N_2{\cdot}GaCl_3$ (**1**), which is stable at room temperature but which eventually decomposes by elimination of 1 mol of $(H_3C)_3SiCl$ at $T > 50$ °C to yield polymeric solid Cl_2GaN_3 (**2**). The analogous I_2GaN_3 was previously synthesized by reactions of GaI_3 and IN_3, and reaction of I_2GaN_3 with liquid bromine yielded Br_2GaN_3.[14] We synthesized compounds **1** and **2** in high yields by means of the procedure summarized as follows:

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients of **1**

	x	y	z	U_{eq}[a]
Ga	9962(1)	2500	1118(1)	36(1)
Cl(1)	9532(1)	4287(2)	2424(2)	57(1)
Cl(2)	1289(1)	2500	577(3)	62(1)
N(1)	9431(4)	2500	8674(8)	35(2)
N(2)	9939(4)	2500	7382(9)	34(2)
N(3)	397(5)	2500	6250(10)	50(2)
Si	8290(1)	2500	8074(3)	38(2)
C(1)	7746(5)	2500	244(14)	69(4)
C(2)	8131(4)	4049(7)	6799(11)	68(2)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ (Å^2 × 10^3).

Table 2. Crystal Data and Structure Determination Details for **1**

empirical formula	$C_3H_9Cl_3GaN_3Si$	Z	4
fw	231.3	T (K)	173
crystal system	orthorhombic	λ(Mo Kα) (Å)	0.710 73
space group	Pnma	ρ_{calc} (g cm^{-3})	1.650
a (Å)	15.823(10)	μ (mm^{-1})	3.09
b (Å)	10.010(5)	R^a (%)	4.2
V (Å^3)	1172.6	$R_w{}^a$ (%)	5.3
Z	4		

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

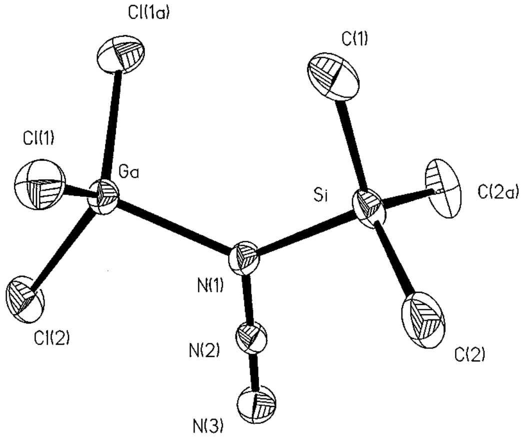
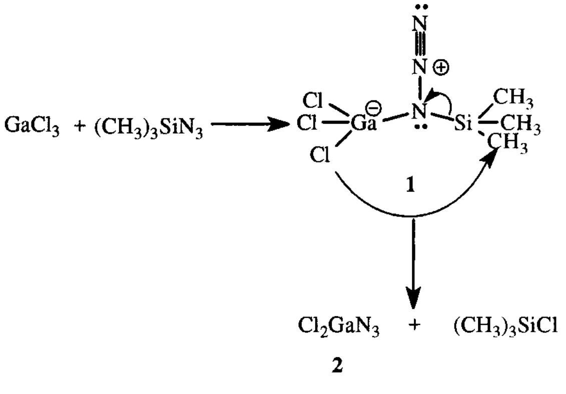


Figure 1. ORTEP diagram of compound **1** showing the atomic labeling scheme. Gallium, Silicon, and the azide group lie on the same plane.



Compound **1** is a highly air-sensitive, low-melting solid (mp 50 °C) that crystallizes by slow sublimation as colorless, well-formed, acicular crystals. An X-ray crystallographic analysis of the material revealed that it is essentially an adduct between $GaCl_3$ and $(H_3C)_3SiN_3$ (Tables 1 and 2). The crystal structure shows the nitrogen atom directly bonded to the silicon (α-nitrogen) to be the electron-donating site in this adduct (Figure 1) as postulated for adducts of group IV organometallic azides and boron tribromide by Thayer and West. In the solid state, **1** essentially consists of monomeric $(H_3C)_3SiN_3{\cdot}GaCl_3$ units in

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Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Ga−N(1)	1.994(6)	N(1)−N(2)	1.250(9)
Si−N(1)	1.859(6)	N(2)−N(3)	1.108(10)
Ga−C(l)1	2.144(2)	Si−C(1)	1.833(7)
Cl(1)−Ga−Cl(2)	113.5(1)	Ga−N(1)−Si	128.7(3)
C(1)−Si−C(2)	112.9(3)	Ga−N(1)−N(2)	115.9(5)
C(2)−Si−C(2a)	115.5(5)	N(2)−N(1)−Si	116.2(5)
C(1)−Si−C(2a)	112.9(3)	Cl(2)−Ga−N(1)	103.7(2)
N(1)−Si−C(1)	104.4(3)	Cl(1)−Ga−Cl(1a)	113.1(1)
N(1)−N(2)−N(3)	179.2(9)	Cl(1)−Ga−N(1)	106.0(1)

which the nitrogens of the azide group and the gallium and silicon atoms lie in the same crystallographic plane. The Ga−N bond distance (1.994 Å) is close to the Ga−N distances (2.04 Å) found for the $[(CH_3)_2GaN_3]_x$ polymeric chain in which the gallium atoms are also connected by the α-nitrogen of the azide group to form a one-dimensional polymer.[15] There are two distinct N−N bond distances in **1**, the longer distance corresponding to the bond between the α-nitrogen (N1) and the middle nitrogen (N2). Furthermore, the Si−C bond length (1.833 Å) is slightly shorter than expected for a single bond, and the Si−N bond length (1.859 Å) is longer than expected for a single bond.

We rationalize these observed bond lengths using the bond valence method, which is routinely applied to analysis of bond lengths in crystal structures[17] but which is less commonly applied to molecular structures (however, see ref 18 for a molecular example). The essence of the method is that a valence, v, is associated with each bond, and this is related to its length, d, by $d = R - b \ln v$. Here b is a "universal" constant, usually taken to be 0.37 Å and R, the *bond valence parameter*, is characteristic of the pair of atoms involved in the bond (in at least a formal sense, R is the length of a single bond for which $v = 1$).[17] The sum of the valences of all the bonds formed by a given atom is equal to the atomic valence V. Extensive tables of bond valence parameters have been given[19] and are used here; of particular interest in the present context is the value $R = 1.49$ Å for the N−N bond and $R = 1.84$ and 1.92 Å for the Ga−N and Ga−C bonds, respectively.

In application to simple azides such as KN_3, bond valence sums show that the appropriate assignment of valences is 5 for the central N atom and 3 for the terminal atoms so the N−N bonds in the symmetrical azide group have $v = {}^5/_2$. The bond length for this valence is expected to be 1.15 Å and for the alkali metal azides is observed to be in the range 1.13−1.18 Å. The remaining bonds from each terminal N atom to the cations have a total strength of ${}^1/_2$ (Figure 2a). In "covalent" azides such as hydrogen azide (Figure 2a) the assignment of valences is $v = 2$ for HN−NN and $v = 3$ for HNN−N. The expected (observed) bond lengths are 1.23 (1.24) and 1.08 (1.12) Å.

In the solid-state structure of dimethylgallium azide shown in Figure 2b, one end of the azide group is bonded to two Ga atoms and the −Ga−N−Ga−N− bonds form a helical chain.[15] The bond valence analysis is simple in this case, and the observed bond lengths (Figure 2b) are close to those expected.

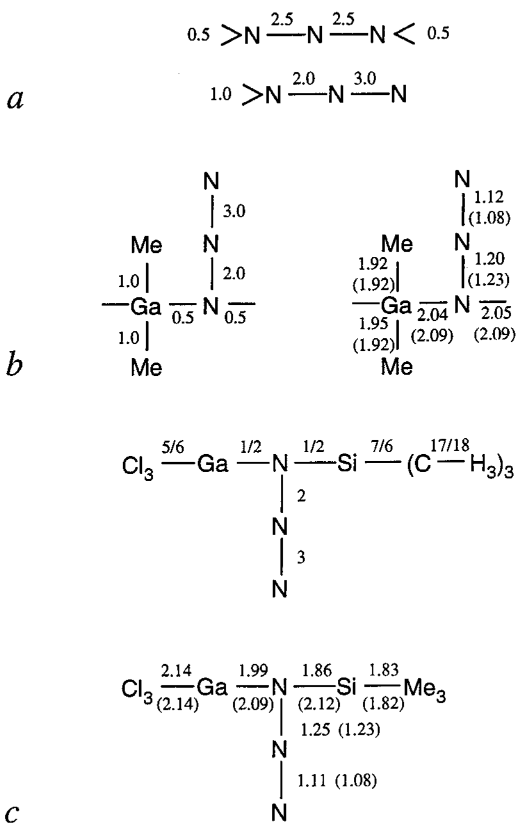

Figure 2. (a) Bond valences in a symmetric azide (top) and in an azide group bonded at one end (bottom). (b) Left: a repeat unit of the dimethylgallium azide structure showing expected bond valences. Right: the same showing observed (expected) bond lengths. (c) Top: expected bond valences in $GaCl_3 \cdot N_3Si(CH_3)_3$. Bottom: the same showing observed (expected) bond lengths.

An apparent weakness of the bond valence method is that it fails to allow for bonding in adducts between two moieties that have fully satisfied valences. For example, the three N−H bonds in NH_3 have a valence of 1 and the bond valence sum at N is the expected 3. Likewise, there are three Ga−C bonds of valence 1 in $Ga(CH_3)$ and the bond valence sum at Ga is 3. According to the bond valence description, no further bonding at N or Ga is expected. Nevertheless, the adduct $(H_3C)_3Ga \cdot NH_3$ forms with a Ga−N bond length of 2.16 Å.[20] The corresponding bond valence for the Ga−N bond is $v = 0.42$. It is important to note, however, that this "extra" bonding is in part compensated by the fact that the Ga−C bond lengths (1.98 Å) are somewhat longer than expected for single bonds (compare Ga−C = 1.93 Å in $(CH_3)_2GaN_3$ discussed above). They correspond to $v = 0.85$, and the bond valence sum at Ga is $0.42 + 3 \times 0.85 = 2.97$, close to the expected 3.0.

In larger molecules, and especially in crystals, the formation of donor−acceptor adducts can be accommodated by further adjustments of bond valences (lengths) as we now illustrate for $(H_3C)_3SiN_3 \cdot GaCl_3$ (**1**). Bond valences in Figure 2c are determined on the basis of an assignment of 0.5 for the valences of the Ga−N and Si−N bonds. In this treatment, Cl and H are underbonded and the ideal valence of 1 for both Cl and H can only be achieved if each H forms an additional bond of $v = {}^1/_{18}$ to Cl. It might be expected therefore that additional weak H−Cl bonds would stabilize the adduct in the crystalline state. Notice that the observed bond lengths are generally close to the expected values; in particular, the Ga−Cl bond lengths are longer than expected (2.07 Å) for a single bond and the Si−C bond lengths are shorter than expected (1.89 Å) as already noted above. The bonds from N to Ga and Si are longer than expected for single bonds (1.84 and 1.77 Å, respectively), but as can be seen from Figure 2c, they are both somewhat shorter (hence stronger) than expected for bonds with $v = {}^1/_2$.

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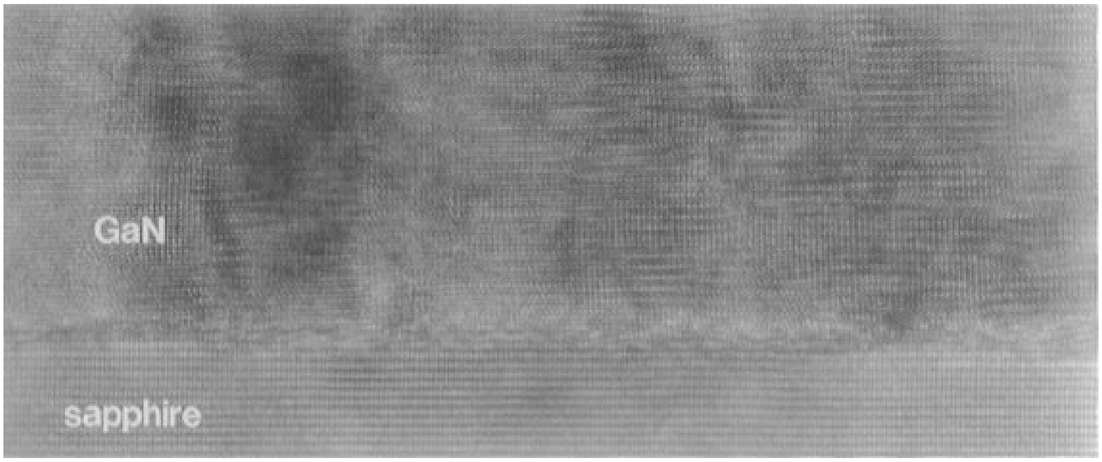

Figure 3. High-resolution TEM image of the wurtzite GaN/sapphire interface showing heteroepitaxial growth.

We further characterized **1** by spectroscopic methods such as FTIR, NMR, and mass spectrometric analysis. The FTIR spectrum reveals the strong N−N−N asymmetric stretch at a frequency of 2170 cm^{-1}, which is not substantially different from that of the free $(CH_3)_3SiN_3$ azide (2160 cm^{-1}). Weak bands corresponding to the C−H symmetric and asymmetric stretches of the $Si(CH_3)_3$ ligand are observed at 2970 and 2900 cm^{-1}, and the strong Ga−Cl stretch is found at 380 cm^{-1}. NMR studies, including ^{1}H and ^{29}Si experiments, confirm the presence of the $Si(CH_3)_3$ group in the molecule, and the ^{29}Si resonance at 44.5 ppm is consistent with tetracoordinate Si. Mass spectrometric analysis of the compound was obtained by direct vaporization of a sample into the mass spectrometer at 30−40 °C and reveals the molecular ion M^+ as the highest peak at 290 amu. Heating of a sample slightly above 50 °C in the mass spectrometer resulted in decomposition of the compound to give gaseous $(CH_3)_3SiCl$, which was detected and identified by its mass spectrum. Continued heating of the sample above 70 °C resulted in evolution of gaseous Cl_2GaN_3 in the form of trimers that ionized to give a spectrum with the highest peaks assigned as $[(Cl_2GaN_3)_3 - Cl]^+$ and $[(Cl_2GaN_3)_3 - N_3]^+$.

2. Synthesis of Cl_2GaN_3 (2). Cl_2GaN_3 (**2**) is obtained in nearly quantitative yields as a colorless air-sensitive solid that is insoluble in organic solvents but sublimes readily at 70−100 °C in vacuum and melts at 210 °C under atmospheric pressure. It is not as air-sensitive as $GaCl_3$ or the gallium trialkyls currently used as precursors in GaN CVD processes. It reacts rapidly but mildly with water and is not sensitive to shock. Elemental analysis for chlorine gave the expected amount in accordance with the proposed empirical formula. The FTIR spectrum is very simple and indicates a polymeric structure similar to that of I_2GaN_3.[14] The spectrum shows the strong asymmetric azide stretch at 2184 cm^{-1} and the Ga−N and Ga−Cl stretches at 450 and 385 cm^{-1}, respectively. The remaining bands at 348 and 250 cm^{-1} are indicative of bridging N−Ga−N modes, consistent with an azide bridging polymer. Electron impact mass spectrometry shows $[(Cl_2GaN_3)_3 - Cl]^+$ and $[(Cl_2GaN_3)_3 - N_3]^+$ as the highest mass peaks at 511 and 506 amu, respectively, and a fragmentation pattern consistent with the proposed trimeric structure.

The physical and chemical properties suggest that the compound is a polymer in the solid state. The Cl_2GaN_3 repeating units are likely to form a chain in which the gallium atoms are linked by the α-nitrogen of the azide group. As a result, the material does not have an appreciable vapor pressure at room temperature but heating at 70 °C in vacuum results in formation of gaseous $(Cl_2GaN_3)_3$ trimers.

3. GaN Growth from Cl_2GaN_3 (2) and $(H_3C)_3SiN_3{\cdot}GaCl_3$ (1). We have used Cl_2GaN_3 (**2**) as a unimolecular precursor to deposit crystalline, highly oriented GaN heteroepitaxially on basal-plane sapphire and on (100) Si substrates at 650−700 °C by UHV CVD. The compound decomposes in our UHV CVD reactor via elimination of $GaCl_3$ and N_2 to produce stoichiometric GaN films, as illustrated in the proposed decomposition reaction.

$$(Cl_2GaN_3)_3 \rightarrow 2GaCl_3 + GaN + 4N_2$$

The GaN films were characterized for elemental composition and thickness by Rutherford backscattering spectroscopy (RBS) as well as Auger and RBS oxygen−carbon resonance profiles, which showed that they were pure and highly homogeneous. High-resolution transmission electron microscopy of cross sections revealed columnar wurtzite material grown on Si and heteroepitaxial single crystalline GaN on sapphire. A typical electron micrograph of the GaN/Al_2O_3 interface demonstrating the heteroepitaxial character of the material and the good crystal quality is shown in Figure 3.

This material represents the first example of a potentially practical, totally inorganic precursor to grow good-quality GaN by low-pressure methods. The deposition procedure was quite simple, involving direct sublimation of the precursor at 70 °C into the hot zone of the reactor in the absence of any carrier gas or toxic ammonia (the reactor pressure is 1×10^{-4} Torr at 70 °C precursor temperature). Current state-of-the-art CVD production of device-quality GaN requires a large excess of NH_3 ranging from 1000−5000-fold. Our method and other similar precursor-related methods have the potential of eliminating the need of NH_3 for GaN growth. Other notable advantages of our method include high growth rates of 50−350 Å/min, low deposition temperatures of 650−700 °C, highly stoichiometric GaN material, and a carbon- and hydrogen-free deposition environment that could be beneficial to p-doping processes.

A potential disadvantage associated with the use of Cl_2GaN_3 (**2**) as a practical source of GaN is that it does not have any significant vapor pressure at room temperature (vacuum-stable at 10^{-7} Torr). This requires heating of the precursor container to 70 °C to obtain sufficient vapor pressure, in addition to turbo-pump processing during growth in order to achieve the low pressures necessary to transport the gaseous precursor. Although substantial growth rates have been achieved under these deposition conditions, higher volatility of the molecule is nevertheless desirable. $(H_3C)_3SiN_3{\cdot}GaCl_3$ (**1**) was also utilized to grow reasonable-quality GaN at approximately 650 °C. However, attempts to increase its vapor pressure by mild heating at 40−50 °C in order obtain sufficient transport of the precursor onto the growth surface resulted in decomposition to $(CH_3)_3SiCl$ and Cl_2GaN_3.

4. Synthesis of Volatile Adducts $Cl_2GaN_3{\cdot}NR_3$ (R = CH_3, C_2H_5). We increased the volatility of Cl_2GaN_3 (**2**) by coordinating the unsaturated monomeric unit with strong Lewis bases to form adducts such as $Cl_2GaN_3{\cdot}NR_3$ (R = CH_3, C_2H_5). The trimethylamine adduct, $Cl_2GaN_3{\cdot}N(CH_3)_3$ (**3**) is a good GaN precursor and is readily prepared by interaction of purified $N(CH_3)_3$ and Cl_2GaN_3 in methylene chloride or hexane at 22 °C. The reaction in methylene chloride produces a waxy residue which, when sublimed at 25−35 °C, yields **3** as a powdery solid that melts sharply at 35 °C. The compound was characterized by elemental analysis for C, H, N, and Cl, the results being consistent with the $C_3H_9Cl_2GaN_4$ empirical formula, and by ^1H NMR, IR, and mass spectrometry. The ^1H NMR spectrum reveals a single resonance (δ 2.72) corresponding to the $N(CH_3)_3$ ligand. IR confirms the presence of $N(CH_3)_3$ by the characteristic C−H stretching bands at 3000−2945 cm^{-1} and shows the symmetric and asymmetric azide stretches at 2110 and 1300 cm^{-1}, respectively. The mass spectra display the expected isotopic envelopes for M^+, (M^+ − Cl), and (M^+ − N_3), the strongest peak, as well as $(Cl_2GaN_3)^+$ and $[N(CH_3)_3]^+$.

The dimethylethylamine adduct $Cl_2GaN_3{\cdot}NC_2H_5(CH_3)_2$ (**4**) is also synthesized by direct treatment of Cl_2GaN_3 with $NC_2H_5(CH_3)_2$ at room temperature. We used the asymmetric dimethylethylamine ligand to promote formation of a liquid precursor, which is often easier to use in CVD processes (asymmetric amines have the propensity to form liquid adducts with aluminum and gallium compounds). The compound is initially obtained as a colorless to pale yellow liquid, but it solidifies during purification by short-path distillation. Its identity was determined by spectroscopic and analytical techniques. The ^1H NMR spectrum shows all of the expected resonances corresponding to amine base ligand. The IR analysis reveals the presence of the azide group with a very strong band at 2110 cm^{-1}, corresponding to the N−N−N asymmetric stretch, and strong bands at 470 and 398 cm^{-1} are due to Ga−N and Ga−Cl stretching modes, respectively. The mass spectrum shows M^+ − Cl and M^+ − N_3 as the highest peaks, and the elemental analysis is consistent with the formula.

5. GaN Growth via Decomposition of $Cl_2GaN_3{\cdot}N(CH_3)_3$ (3). The deposition process is similar to that developed for growth of GaN from Cl_2GaN_3. The CVD reactor used in this study is a cold-wall, inductively-heated system described in detail elsewhere.[16] The precursor is kept in a glass container equipped with a high-vacuum valve, and the container is directly attached to the reactor, which is constantly maintained at 2×10^{-8} Torr by a corrosion-resistant turbo pump. In a typical experiment, the source container valve is opened, resulting in a rapid rise of reactor pressure to approximately 5×10^{-5} Torr. Although film growth has been obtained at this pressure, we heat the precursor to its melting point in order to achieve reasonable growth rates of about 50 Å/min at 2×10^{-4} Torr. Films ranging in thickness from 1000 to 2500 Å are normally deposited at 700 °C on sapphire and Si substrates with rates of 150−200 Å/min. RBS analysis including carbon and oxygen resonances of these films reveals stoichiometric GaN with chlorine and carbon contamination of 1−2 atom % as shown in Figure 4 (carbon and oxygen nuclear resonance reactions allow detection as low as 0.5 atom % C and 1.5 atom % O). Films grown at a slower rate of 50−80 Å/min are pure, as shown by RBS, and they display higher crystal quality, as revealed by TEM examinations.

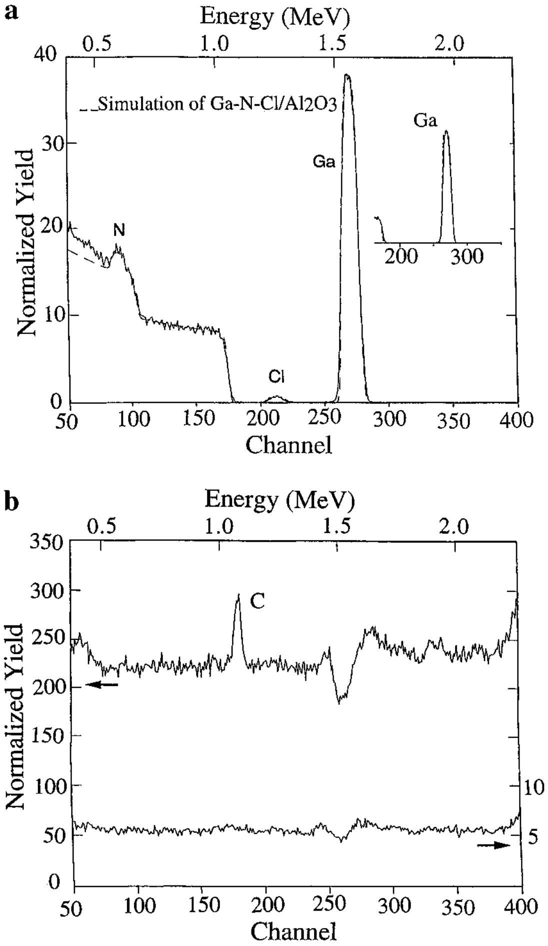

Figure 4. (a) Rutherford backscattering spectrum (RBS) of gallium nitride films deposited on sapphire using $Cl_2GaN_3{\cdot}N(CH_3)_3$ as precursor at 650 °C (160 Å/min) and 700 °C (30−45 Å/min) inset. Films with composition $Ga_{0.95}N_{1.05}$ that contain 2−2.5 atom % Cl contamination are grown at 650 °C, as visible in the spectrum. Stoichiometric GaN with Cl contents lower than the detection limit of RBS (0.5 atom %) is deposited at 750 °C (inset). (b) Corresponding RBS carbon resonance spectra indicating 2.5 atom % C contamination for the 650 °C growth and virtually no carbon contamination for the higher temperature deposition.

Summary

In this paper a new, low-temperature route to stoichiometric GaN featuring a new inorganic precursor, Cl_2GaN_3, that is entirely free of carbon and hydrogen is demonstrated, and syntheses of Lewis base adducts of the precursor polymer with trialkylamines are described. The trimethylamine adduct, $Cl_2GaN_3{\cdot}N(CH_3)_3$, is a more convenient precursor to GaN than Cl_2GaN_3 because it is substantially more volatile and therefore easier to utilize in CVD processes. High-quality wurtzite GaN was been grown by thermal decomposition of $Cl_2GaN_3{\cdot}N(CH_3)_3$ (**3**) at 650−700 °C. En route to Cl_2GaN_3 (**2**), by reaction of $(CH_3)_3SiN_3$ and $GaCl_3$, the monomeric adduct $(H_3C)_3SiN_3{\cdot}GaCl_3$ (**1**) was isolated and was then characterized by single-crystal X-ray analysis. The structure analysis confirms that the α-nitrogen of the azide ligand is the electron-donating site of the adduct.

Experimental Section

General Procedures. Reactions were performed under prepurified nitrogen with standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl prior to use. ^1H (300 MHz) and ^{13}C (125.7 MHz) NMR spectra were collected on a Varian Gemini 300 spectrometer and were referenced to the solvent resonances (C_6D_6;

^{1}H δ 7.17; ^{13}C δ 128.0). FTIR spectra were recorded on a Nicolet Magna-IR spectrometer either in Nujol mull or in a 10-cm gas cell with KBr windows. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). Electron impact mass spectra were collected on a Finnigan-MAT Model 312 mass spectrometer (IE = 70 eV, source T = 225 °C). Gallium trichloride (Aldrich) was used as received. Trimethylsilyl azide (Aldrich) was purified and distilled, and the amines (trimethylethyl and trimethyl) (Aldrich) were purified over P_2O_5 and then distilled.

Synthesis of $(H_3C)_3SiN_3{\cdot}GaCl_3$ (1). To a solution of $GaCl_3$ (4.1 g, 23.3 mmol) in hexane (80 mL) was added $(H_3C)_3SiN_3$ (2.69 g, 23.4 mmol) at −196 °C. The mixture was slowly allowed to reach ambient temperature and stirred for 12 h. The resulting suspension was allowed to settle, and the solvent was filtered. The remaining solid was extracted several times with dry hexane, and the resulting filtrates were combined and cooled overnight at −5 °C to produce a colorless crystalline solid. Concentration and cooling of the solution provided several additional crops of crystals to give a total yield of 5.2 g (77%); mp 50 °C. IR (Nujol): 3343 (w), 2397 (w), 2166 (vs), 1268 (s), 1200 (s), 1058 (s), 848 (s), 796 (m), 764 (m), 638 (w), 560 (w), 380 (vs) cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 0.61. ^{29}Si NMR (solid state): 44.5 ppm. EIMS (m/z): 290 (M$^+$).

Structure of $(H_3C)_3SiN_3{\cdot}GaCl_3$ (1). Air- and moisture-sensitive crystals of $(H_3C)_3SiN_3{\cdot}GaCl_3$ were mounted under N_2 and sealed in X-ray capillary tubes. A suitable specimen was mounted vertically and immediately centered optically on a Siemens P4 autodiffractometer equipped with an LT-2a temperature controller preset at 100 °C. A random search quickly located 25 reflections with $15° < 2\theta < 30°$. Autocentering of these reflections revealed a primitive orthorhombic cell. A quarter of the hemisphere of the data was collected out to $2\theta = 50°$. Analysis of the systematic absences showed a choice between the space groups $Pna2_1$ and $Pnma$. The structure was solved in both symmetries, but the centrosymmetric $Pnma$ group gave the best refinement with no correlation in the least-squares cycles. An absorption correction was performed using empirical ψ scan data. Structure solution was performed using direct methods, showing the Ga and Si atoms to lie in mirror planes. Subsequent cycles of refinement and difference maps led to the location of the remaining non-hydrogen atoms in the asymmetric unit; all non-hydrogen atoms were modeled anisotropically and the H atoms were positioned in a riding model with fixed C−H distances and isotropic thermal parameters. Convergence led to final R/R_w values of 0.043/0.053 with 729 data ($F > 10\sigma(F)$) and 61 parameters. All data reduction, solution, and refinement calculations utilized the SHELTEXT Plus package of programs available from Siemens Analytical X-ray Co., Madison, WI.

Synthesis of Cl_2GaN_3 (2). To a frozen solution of $GaCl_3$ (15.0 g, 85.2 mmol) in CH_2Cl_2 (80 mL) at −196 °C was added $(CH_3)_3SiN_3$ (11.3 mL, 85.1 mmol) by syringe. The mixture was allowed to slowly warm to room temperature and stirred for 18 h. The CH_2Cl_2 was removed under reduced pressure, and the residue was sublimed (115 °C, 10−5 Torr) to give 14.5 g (79.5 mmol, 93%) of Cl_2GaN_3 as a white powder; mp 209−211 °C. IR (Nujol): 3359 (w, $\upsilon_{as}(N_3) + \upsilon_s(N_3)$), 2403 (m, $2 \times \upsilon_s(N_3)$), 2184 (vs, $\upsilon_{as}(N_3)$), 1205 (vs, $\upsilon_s(N_3)$), 1097 (w, combn), 759 (s, $\delta(N_3)$), 551 (m, $\gamma(N_3)$), 452 (s, υ(MN)), 429 (s, υ(MN)), 383 (s, υ(MCl)), 348 (m, δ(NMN)), 250 (s, δ(NMN)) cm^{-1}. EIMS (m/z): 511 [$(Cl_2GaN_3)_3 - Cl$)] and 506 [$(Cl_2GaN_3)_3 - N_3$)]. Anal. Calcd for Cl_2GaN_3: Cl, 38.8. Found: Cl, 37.96.

Synthesis of $Cl_2GaN_3{\cdot}N(CH_3)_3$ (3). Dry trimethylamine (1.61 g, 27.3 mmol) was condensed at −196 °C into a suspension of freshly sublimed **2** (5.0 g, 27.3 mmol) in CH_2Cl_2 (60 mL). The mixture was stirred for 24 h at 22 °C, at which point all the solid had dissolved. The volatiles were then removed under vacuum to yield 6.4 g of a waxy material that was sublimed at 30 °C and 10^{-3} Torr to produce a colorless solid; mp 35 °C. ^{1}H NMR (C_6D_6, 25 °C) δ 2.72. IR (KBr) 3397 (w, $\upsilon_{as}(N_3) + \upsilon_s(N_3)$), 2998−2946 (w, C−H str), 2104 (vs, $\upsilon_{as}(N_3)$), 1473 (m), 1425 (w), 1352 (w), 1299 (m, $\upsilon_s(N_3)$), 1268 (m), 1115 (w), 982 (m), 900 (m), 815 (m), 674 (m), 530 (w), 457 (m), 399 (s) cm^{-1}. EIMS (m/z): 242 (M$^+$), 205−207 (M$^+$ − Cl), 200 (M$^+$ − N_3), 184 [M$^+$ − $N(CH_3)_3$], 141 ($GaCl_2^+$), 105 ($GaCl^+$), 69 (Ga^+), 59 [$N(CH_3)_3^+$]. Anal. Calcd for $Cl_2GaN_3{\cdot}N(CH_3)_3$: C, 14.93; H, 3.76; N, 23.23; Cl, 29.4. Found: C, 14.9; H, 3.87; N, 21.20; Cl, 30.4.

Synthesis of $Cl_2GaN_3{\cdot}NC_2H_5(CH_3)_2$ (4). Dry dimethylethylamine (4.56 g, 62.30 mmol) was added to a suspension of **2** (11.40 g, 62.30 mmol) in methylene chloride (80 mL). The mixture was stirred at room temperature for 2 h at which point all the solid had dissolved. The solvent was removed in vacuo, yielding a pale yellow liquid. ^{1}H NMR (C_6D_6, 25 °C): δ 1.32 (3H, t, J = 7.20 Hz, CH_2CH_3), 2.71 (6H, s, CH_3), 3.14 (2H, q, J = 7.20, CH_2). IR (liquid film): 3386 (m, $\upsilon_{as}(N_3) + \upsilon_s(N_3)$), 3000−2953 ($\upsilon$(C−H)), 2115 (vs, $\upsilon_{as}(N_3)$), 1297 (vs, $\upsilon_s(N_3)$), 1186 (s), 1110 (s), 1090 (m), 1938 (s), 995 (s), 779 (vs), 669 (m), 605 (m), 537 (s) 470 (s, υ(GaN)), 398 (vs, υ(GaCl)) cm^{-1}. EIMS (m/z): 214 (M$^+$ − N_3). Anal. Calcd for $Cl_2GaN_3{\cdot}N(CH_3)_2C_2H_5$: C, 18.8; H, 4.3. Found: C, 18.8; H, 4.7.

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Supporting Information Available: Listings of crystallographic experimental details, hydrogen atomic coordinates, equivalent isotropic displacement coefficients, and complete bond distances and angles for the non-hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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