Formation of a Tetrameric, Cyclooctane-like, Azidochlorogallane, $[HClGaN_3]_4$, and Related Azidogallanes. Exothermic Single-Source Precursors to GaN Nanostructures

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Abstract: The synthesis of a novel tetrameric gallane, $[HClGaN_3]_4$ (**1**), with a heterocyclic cyclooactane-like structure has been demonstrated. A single-crystal X-ray study reveals that the molecule consists of eight-membered Ga_4N_4 rings with Ga atoms bridged by the α-nitrogens of the azide groups. $[HClGaN_3]_4$ crystallizes in the tetragonal space group space group $P4_2bc$, with $a = 17.920(3)$ Å, $c = 10.782(3)$ Å, $V = 3462(2)$ Å^3, and $Z = 8$. On the basis of the mass spectrum, the vapor of the compound consists of the trimer $[HClGaN_3]_3$, which is a low-temperature molecular source for growth of GaN layers on sapphire and Si substrates at 500 °C. Solid **1** decomposes exothermically at 70 °C to yield bulk nanocrystalline wurtzite and zinc blende GaN. The reaction between H_2GaCl and LiN_3 yields the analogous and extremely simple azidogallane $(H_2GaN_3)_n$ (**2**), which is used to deposit crystalline GaN films at 450 °C. Compound **2** is considerably more reactive than **1**, and its decomposition, often initiated at room temperature, yields pure and crystalline nitride material of unusual morphology and microstructure.

Introduction

The importance of GaN and related wide band gap nitrides in the successful fabrication of light-emitting diodes and semiconductor lasers has prompted considerable research into their growth and development.[1−3] Currently, the most common route to deposition of GaN by chemical vapor deposition (CVD) employs reactions of $(CH_3)_3Ga$ and $(C_2H_5)_3Ga$ with a large excess of ammonia at temperatures in excess of 1000 °C.[4] Alternative synthetic methods based on single source molecular precursors that incorporate direct Ga−N bonds and labile, preferably, nonorganic leaving groups offer the potential of significant improvements in film quality and growth process.[5] Some of these benefits include lower deposition temperature, elimination of the inefficient use of ammonia, reduction in nitrogen vacancies and carbon contamination, and much enhanced doping capabilities.

Recently, we demonstrated that the decomposition of an exclusively inorganic precursor, Cl_2GaN_3, leads to thin, oriented GaN layers on (100) Si substrates and heteroepitaxial films on basal plane sapphire at 700 °C.[6,7] The probable decomposition pathway is demonstrated by eq 1. Other azide-containing

$$(Cl_2GaN_3)_3 \rightarrow GaN + 2GaCl_3 + 4N_2 \quad (1)$$

compounds that have been utilized to deposit GaN films contain organic groups and in many cases lead to unintentional incorporation of carbon impurities.[8−10]

In search of new and more advantageous precursors for GaN growth, we have focused our efforts on development of $HClGaN_3$ (**1**), a novel completely inorganic azide analogous to Cl_2GaN_3. The chloride and hydride ligands in this new system offer the possibility for elimination of HCl rather than $GaCl_3$ and thus provide a simple, low-temperature route to high-yield stoichiometric material. In this paper we describe the synthesis and characterization of **1**, and the related $(H_2GaN_3)_n$ (**2**), as well as the utility of these compounds as precursors for synthesis of GaN thin films and bulk material. The simplicity of **1** and **2** (they are typical examples of classical inorganic compounds) and their exothermic reactivity driven by elimination of extremely stable species such as H_2, N_2, and HCl to form GaN are potentially appealing from both a fundamental and a practical viewpoint.

Results and Discussion

The synthesis of **1** was accomplished via a metathesis reaction involving $HGaCl_2$ and LiN_3. $HGaCl_2$ has been previously prepared according to reaction 2.[11] Interactions of this compound with rigorously dried LiN_3 at 20 °C, followed by removal

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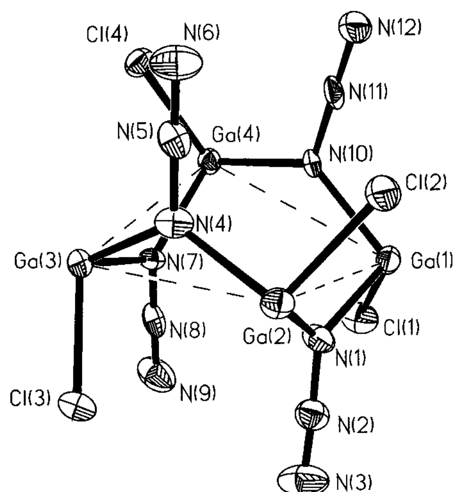

Figure 1. Molecular structure of the azidochlorogallane $[ClHGaN_3]_4$ (**1**) displaying the eight-membered ring structure.

of the volatiles, result in a waxy solid that is readily crystallized in hexane to give a colorless solid in typically 85% yield based on eq 3. The elimination of LiCl is quantitative, and its identity

$$GaCl_3 + SiMe_3H \rightarrow HGaCl_2 + SiMe_3Cl \qquad (2)$$

$$HGaCl_2 + LiN_3 \rightarrow HClGaN_3 + LiCl \qquad (3)$$

is readily established by powder X-ray diffraction. A complete elemental analysis (for C, H, Cl, Ga, and N) of the product indicated the formula $HClGaN_3$ and revealed lack of any measurable carbon impurities.

An X-ray crystallographic analysis reveals that the compound in the solid state consists of tetrameric $[HClGaN_3]_4$ units with a conformation similar to cyclooctane (Figure 1). The tetramer is formed by four Ga atoms bridged by the α-nitrogen of the azide groups, and the nonbridging positions are occupied by alternating up and down Cl atoms. Structures that contain Ga centers connected by the α-nitrogen of an azide group have been demonstrated for the polymeric chain $(Me_2GaN_3)_x$[12] and for the Lewis acid−base adduct $(H_3C)_3SiN_3{\cdot}GaCl_3$.[7] Interestingly, the bis(dimethylamido)gallium azide, $(Me_2N)_2GaN_3$, was shown to consist of dimers formed by bridging dimethylamido (Me_2N) groups rather than azide ligands.[9] $HClGaN_3$, however, is the first proven example of a Ga molecular ring system formed by means of bridged azides, although such structures have been suggested for the trimers $[(C_2H_5)_2GaN_3]_3$ and $[(C_2H_5)_2AlN_3]_3$ in solution.[13,14] The Ga_4N_4 cyclic core of **1** has intramolecular Ga−Ga distances (the distances between azide-bridged Ga atoms) ranging from 3.49 to 3.52 Å. The Ga−N and Ga−Cl distances vary from 1.918 to 2.063 and 2.134 to 2.184 Å, respectively. However, there are two distinct N−N bond distances, the shorter corresponding to the terminal N−N moiety of the azide group (Tables 1 and 2). This terminal bond is shorter by about 0.1 Å, and it implies a considerably activated azide toward elimination of N_2. The tetramers form extended zigzag chains via dative interactions between a terminal Cl atom and the neighboring Ga atom (Figure 2). The intermolecular Ga−Cl distances range from 3.53 to 3.73 Å. A notable feature of the long range structure is that only adjacent Ga atoms in the ring participate in the intermolecular interactions that are responsible for the formation of the chains (Figure 2).

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Table 1. Selected Distances (Å) and Angles (deg) for $(HClGaN_3)_4$

Distances

Ga(1)−Cl(1)	2.134 (11)	Ga (1)−N(1)	2.063 (16)
Ga (1)−N (10)	1.951 (14)	Ga (2)−Cl (2)	2.184 (5)
Ga (2)−N (1)	1.918 (17)	Ga (2)−N (4)	1.970 (15)
Ga (3)−Cl (3)	2.183 (9)	Ga (3)−N (4)	1.994 (15)
Ga (3)−N (7)	1.951 (17)	Ga (4)−Cl (4)	2.178 (5)
Ga (4)−N (7)	1.987 (14)	Ga (4)−N (10)	2.023 (16)
N (1)−N (2)	1.233 (19)	N (2)−N (3)	1.127 (22)
N (4)−N (5)	1.236 (19)	N (5)−N (6)	1.132 (21)
N (7)−N (8)	1.254 (19)	N (8)−N (9)	1.150 (21)
N (10)−N (11)	1.257 (19)	N (11)−N (12)	1.115 (21)

Angles

Cl (1)−Ga (1)−N (1)	100.4 (5)	Cl (1)−Ga (1)−N (10)	103.4 (6)
N (1)−Ga (1)−N (10)	97.8 (6)	Cl (2)−Ga (2)−N (1)	103.8 (5)
Cl (2)−Ga (2)−N (4)	100.1 (4)	N (1)−Ga (2)−N (4)	99.4 (8)
Cl (3)−Ga (3)−N (4)	98.1 (6)	Cl (3)−Ga (3)−N (7)	103.3 (4)
N (4)−Ga (3)−N (7)	97.6 (6)	Cl (4)−Ga (4)−N (7)	98.7 (5)
Cl (4)−Ga (4)−N (10)	98.4 (5)	N (7)−Ga (4)−N (10)	97.4 (7)
Ga (1)−N (1)−Ga (2)	123.5 (7)	Ga (1)−N (1)−N (2)	115.0 (12)
Ga (2)−N (1)−N (2)	120.8 (13)	N (1)−N (2)−N (3)	176.5 (18)
Ga (2)−N (4)−Ga (3)	124.6 (7)	Ga (2)−N (4)−N (5)	116.7 (11)
Ga (3)−N (4)−N (5)	118.7 (11)	N (4)−N (5)−N (6)	175.6 (19)
Ga (3)−N (7)−Ga (4)	124.5 (6)	Ga (3)−N (7)−N (8)	118.4 (11)
Ga (4)−N (7)−N (8)	116.8 (12)	N (7)−N (8)−N (9)	178.1 (20)
Ga (1)−N (10)−Ga (4)	124.6 (7)	Ga (1)−N (10)−N (11)	119.7 (11)
Ga (4)−N (10)−N (11)	115.2 (11)	N (10)−N (11)−N (12)	178.9 (20)

Table 2. Crystal Data for $(HClGaN_3)_4$ (**1**) at −100 °C

space group: $P4_2bc$	mol wt = 148.2
a =17.920 (3) Å	ρ_{calcd} = 2.28 g cm^{-3}
c = 10.782 (3) Å	μ_{calcd} = 6.78 mm^{-1}
V = 3462 (2) Å^3	size = 0.2 × 0.2 × 0.4 mm
Z = 8	GOF = 1.96

diffractometer: Siemens P4
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.170 73 Å
monochromator: graphite crystal, $2\theta = 12°$
scan range, type: $3° < 2\theta < 50°$
scan speed, width: variable 3−15.00°/min in ω
rflctns: 3432 total, 1628 independent, 1344 ($(F) > 3\sigma(F)$)
R_{int}: 4%
final R indices: $R = 0.0520$; $R_w = 0.0564$
all data: $R = 0.0660$, $R_w = 0.0605$

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

The infrared spectra include vibrations at 2115 cm^{-1} [$\nu_{as}(N_3)$], 1990 cm^{-1} [ν_{as}(Ga−H)], 1243 cm^{-1} [ν_s(N3)], 575 cm^{-1} (Ga−H deformations), 406 cm^{-1} [ν_{as}(Ga−Cl)], and 334 cm^{-1} (Ga−N−Ga bridging modes). The ^{1}H NMR spectrum of the compound dissolved in toluene-d_8 at 20 °C consists of a broad peak at δ 5.25, a shift characteristic of terminal Ga−H groups. The broadening is attributed to the quadrupolar Ga nuclei. This resonance becomes considerably sharper at −50 °C, but the spectrum is otherwise unchanged. The mass spectra displayed isotopic envelopes for $M_3^+ - H$ as the highest mass peak at 443 amu (M = $HClGaN_3$) as well as mass peaks for (M_3^+ − Cl), ($M_3^+ - N_3$), M_2^+, and M^+. The calculated isotopic patterns are in excellent agreement with the experiment and support the proposed trimeric gas-phase structure.

Compound **1** is stable with respect to loss of HCl and N_2 at room temperature. It is insensitive to shock, but it decomposes exothermically at the melting point (70 °C) via displacement of N_2 and HCl to yield a light gray solid. The decomposition occurred very rapidly with release of large amounts of heat, and often with spontaneous ignition. The solid was identified by powder X-ray diffraction and by IR examination to be nanocrystalline GaN. The IR spectra illustrated a broad peak at 560 cm^{-1} corresponding to Ga−N lattice vibrations and

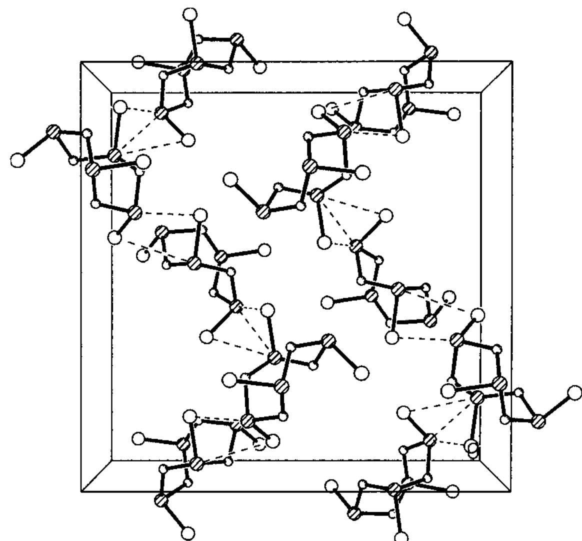

Figure 2. Stereoview of the unit cell contents showing the extended chains formed by cyclic tetramers that are bridged by Cl atoms. The intermolecular Ga---Cl distances range from 3.53 to 3.74 Å.

showed no detectable azide, Ga−H, N−H, and O−H absorptions. Complementary transmission electron microscope studies confirmed that the material was nanocrystalline, with a mixture of cubic and hexagonal GaN grains. As indicated earlier, the precursor was volatile in the mass spectrometer at room temperature and the spectrum indicated that the vapor consisted of the trimer $[HClGaN_3]_3$. We performed vapor deposition studies, and initial results clearly showed that the thermal decomposition of the vapor on sapphire substrates at 500−550 °C resulted in formation of stoichiometric GaN. Relatively low chlorine contamination (0.5 at. %) was found for films grown at and below 500 °C, but higher deposition temperatures (600 °C) provided material free of chlorine impurities.

The successful synthesis of **1** prompted the development of the related but simpler $(H_2GaN_3)_n$ (**2**), which offers the possibility of GaN synthesis much more efficiently, by displacement of the noncorrosive and relatively innocuous (at least to the growth process) H_2 and N_2 byproducts. This carbon- and halide-free molecule is particularly attractive as a precursor to high-purity bulk material for GaN crystal growth at high pressures using the multianvil method. In addition to the lack of carbon and halide groups, another unique aspect of this system is the lack of strong N−H bonds, which facilitate loss of nitrogen as NH_3, thus leading to nonstoichiometric nitride material. The decomposition of the similar $(H_2GaNH_2)_3$ compound is reported to occur via loss of NH_3 and H_2 to yield material with the formula $GaN_{0.83}$.[15]

The preparation of **2** utilized the interaction of freshly prepared H_2GaCl[16]with LiN_3 to yield a colorless liquid and a stoichiometric amount of LiCl (eq 4). The IR spectrum of the

$$H_2GaCl + LiN_3 \rightarrow H_2GaN_3 + LiCl \qquad (4)$$

product displays two distinct and very intense bands at 2130 and 1980 cm^{-1}, assigned $\nu_{as}(N_3)$ and ν_{as}(Ga−H), respectively. Other notable features include $\nu_{sym}(N_3)$ at 1238 cm^{-1}, ν(Ga−N) at 475 cm^{-1}, ν(N−Ga−N) at 345 cm^{-1} and a strong absorption at 710−675 cm^{-1} corresponding to GaH_2 scissoring deformations (Figure 3). The last is very prominent in molecules containing terminal Ga−H_2 units such as $(H_2GaCl)_2$[16] and $(Me_2NGaH_2)_2$,[17,18] but it is not observed in the spectrum of $(HClGaN_3)_4$ (**1**). The weak bands at 3360 and 2470 cm^{-1}, as visible in Figure 3, are overtones and correspond to $\nu_{as}(N_3) + \nu_{sym}(N_3)$ and 2 × $\nu_{sym}(N_3)$, respectively. These features are common for organometallic azides of Al, Ga, and In and have been previously observed in the IR spectra of X_2MN_3 (X = Cl, Br, I and M = Al and Ga).[14,19]

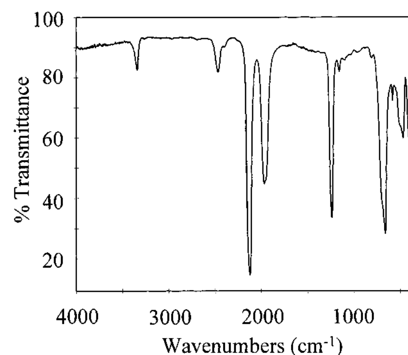

Figure 3. Infrared spectrum of $(H_2GaN_3)_n$ as a thin film on KBr plates. The sharp overtones at 3360 and 2470 cm^{-1} are $\nu_{as}(N_3) + \nu_{sym}(N_3)$ and 2 × $\nu_{sym}(N_3)$, respectively.

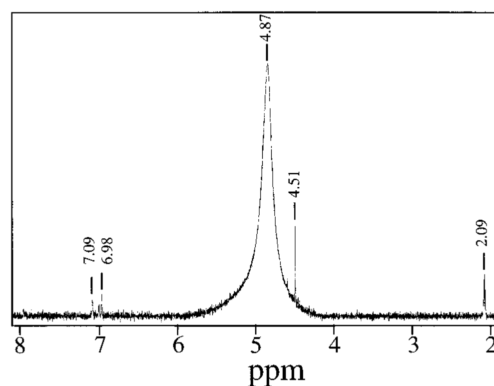

Figure 4. ^{1}H NMR spectrum of $(H_2GaN_3)_n$ at 20 °C of the sample dissolved in toluene-d_8. The resonance at δ 4.51 is due to dissolved H_2 resulting from a minor decomposition of the compound. The analogous spectrum in THF-d_8 does not show any decomposition even after 24 h. The resonances near δ 7.09, 6.98, and 2.09 are due to residual toluene in the solvent.

The ^{1}H NMR spectrum at 20 °C in toluene-d_8 revealed a rather broad Ga−H resonance at δ 4.87, a value significantly different than that found for **1** (δ 5.25) and for H_2GaCl (δ 5.40).[16] The peak sharpens considerably at −50 °C, but its position remains the same. After several hours, at room temperature an additional sharp peak was observed at δ 4.51 and was accompanied by formation of a very small amount of a white precipitate (Figure 4). This feature at δ 4.51 has been previously attributed to dissolved H_2, and its presence suggests minor decomposition with loss of hydrogen.[20] In contrast, the ^{1}H NMR spectrum in THF-d_8 shows a single, relatively sharp, resonance at δ 4.86 and does not indicate any dissolved H_2 or precipitate formation for solutions that remained at room temperature for several days, indicating that a THF complex of the compound may be responsible for the remarkable stability

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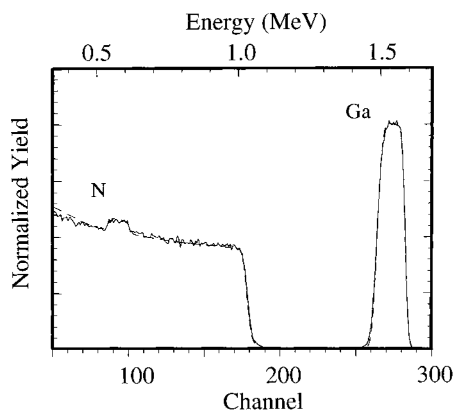

Figure 5. 2 MeV He^{2+} RBS spectrum of GaN on (100) Si. Simulation of the composition using the program RUMP (dotted line) indicates stoichiometric GaN material free of Cl impurities.

of H_2GaN_3 over time. The mass spectrum displays the calculated isotopic patterns for the ions $(H_2GaN_3)^+$ at 114 amu, $[(H_2GaN_3)_2{}^+ - H]$ at 227 amu, $[Ga_3N_9]$ at 334, and $[(H_2GaN_3)_3{}^+ - H_2]$ at 340 amu.

Initial results indicate that compound **2** in its pure form is extremely reactive at room temperature. Its decomposition, frequently induced by scraping the sample in the drybox by a glass or metal rod, is very characteristic of a self-sustaining exothermic reaction rather than a detonation. This high reactivity made it impossible to obtain combustion analysis, although the decomposition byproducts were characterized as we describe below. The compound was nevertheless easily handled in solution, and its role as a potential precursor to GaN thin films and bulk materials was explored. We performed depositions on Si substrates by direct vaporization of the compound in an ultrahigh-vacuum chemical vapor (UHV−CVD) deposition system to illustrate the feasibility of the molecule as a CVD precursor. Film growth was obtained at $(2-4) \times 10^{-4}$ Torr and 450 °C with a deposition rate of 12 nm/min. Rutherford back-scattering (RBS) including carbon, oxygen, and nitrogen resonance reactions reveal pure and stoichiometric GaN material (Figure 5). Cross-sectional high-resolution TEM observations showed growth of columnar grains, typically about 50 nm wide, that extended from the interface through the entire layer and consisted of completely crystalline material. Both wurtzire and zinc blende regions could be identified from their characteristic stacking sequences. The most noteworthy highlight of this preliminary study is the extensive crystallinity observed (no amorphous areas were found) for a material that is not epitaxial since it is grown on native Si oxide and below 450 °C, as shown in Figure 7.

Equally fascinating was the unusual morphology and microstructure of the highly pure bulk GaN material obtained from the rapid decomposition of the precursor often initiated at or near room temperature in the drybox. The material is composed of a light yellow network of interconnected microfibers up to several microns in length and 15−20 nm wide that consist of crystallites oriented along the fiber axis (Figure 6). Interestingly, we did not observe any amorphous component by TEM neither at the grain boundaries nor in the bulk of the fibrous material. The individual grains that ranged from 15 to 20 nm in size were primarily hexagonal GaN, although disordered regions and some of the cubic phase were also found. The polycrystalline character of this high aspect ratio product and the presence of the cubic and hexagonal phases were confirmed by X-ray diffraction studies, which also demonstrated the preferential orientation of the crystallites. The only feature displayed in

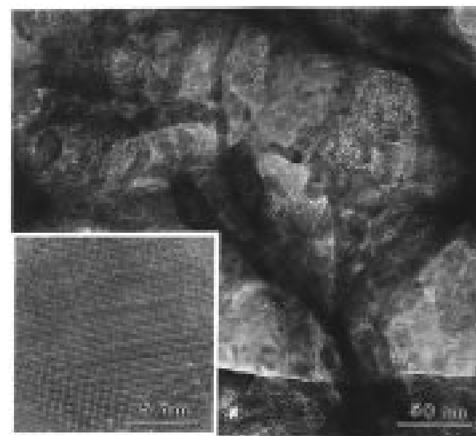

Figure 6. Electron micrograph showing the nanocrystalline fibrous nature of GaN powder formed by the decomposition of $(H_2GaN_3)_n$. Thje inset shows the highly enlarged view of individual crystallites. The direction of the lattice fringes follows the orientation of the fiber.

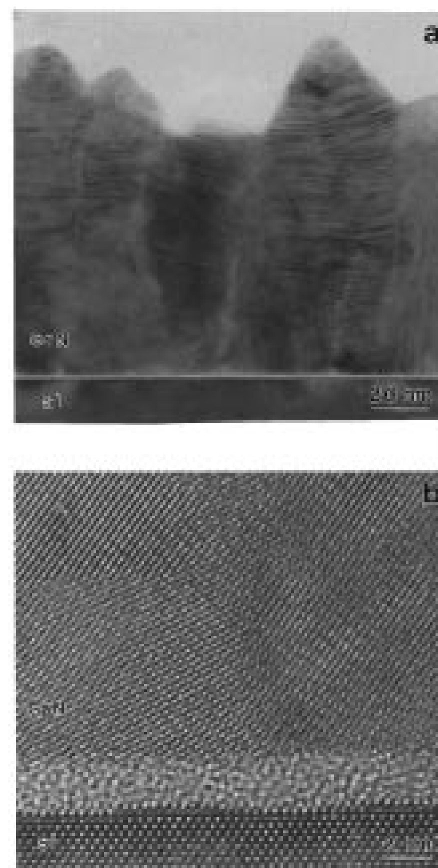

Figure 7. (a) Cross-sectional electron micrograph showing columnar growth of mixed cubic and hexagonal phases on oxidized (amorphous layer) Si (100) substrate. (b) High magnification image showing growth of the wurtzite phase close to the substrate.

the IR spectra was a remarkably sharp band at 560 cm^{-1}, consistent with crystalline GaN. The lack of O−H modes in the IR spectra even after prolonged exposures (several weeks) to air demonstrates the high stability of this high surface area material. Furthermore, energy-dispersive X-ray analysis in a field emission gun microscope did not show any chlorine contamination, indicating that the precursor did not contain chlorine impurities. Annealing of the microfibers at 800 °C produced a completely white powder that was found to be wurtzitic GaN by powder diffraction. Photoluminescence

studies show that the annealed material luminesces at about 3.3 eV whereas the unannealed sample emits in the visible (1.92 eV) and UV regions (3.28 eV).[21]

Concluding Remarks

The extremely simple inorganic gallanes $(HClGaN_3)_4$ (**1**) and $(H_2GaN_3)_n$ (**2**) offer a new, very-low-temperature method for synthesizing bulk, polycrystalline GaN microfibers and thin films. A range of analytical and crystallographic data as well as optical studies are clearly consistent with a high-purity mixture of wurtzite and zinc blende phases with unusual nanosize morphologies. In semiconductors, such morphologies have recently gained considerable attention because of their possible uses in optoelectronics and nanodevices. In addition to their unique application in GaN synthesis (in their present and rather unstable form), of immediate interest is the preparation of potentially more stable Lewis acid−base complexes that could lead to the development of a new class of GaN precursors. Especially instructive is the unique octagonal boatlike structure of **1**, which unequivocally demonstrates that inorganic azides of the group 13 metals form ring structures with bridging azide ligands. The Ga_4N_4 framework found here for **1** is not very common, although a similar structure containing eight-membered Al_4F_4 puckered rings has been proposed for the gaseous $[(CH_3)_2AlF]_4$ compound.[22] More common is the trimeric cyclohexane-like conformation that has been shown to exist in the solid-state structure of the trimeric $(Cl_2BN_3)_3$.[23]

Our attempts to use these compounds for deposition of heteroepitaxial, device-quality GaN thin films will be reported in due course. Preparation of GaN nanostructures in solution by a catalyzed decomposition of **2**, using transition metal complexes that promote controlled evolution of N_2 and H_2, is currently being investigated.

Experimental Section

General Considerations. Reactions were performed under pre-purified nitrogen using standard Schlenk and drybox techniques. Dry, air-free solvents were distilled from sodium benzophenone ketyl prior to use. ^1H (300 MHz) NMR spectra were recorded on a Varian Gemini 300 and a Varian Unity 500 spectrometer and referenced to the solvent resonances (C_6D_6, ^1H δ 7.15). FTIR spectra were recorded on a Nicolet Magna-IR 550 spectrometer either as a Nujol mull between KBr plates or in a 10 cm gas cell with KBr windows. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Electron impact mass spectra were performed on a Finnigan-MAT Model 312 mass spectrometer (IE = 70 eV, source T = 20 °C) in the ASU departmental mass spectrometry facility. Gallium trichloride (Aldrich) and trimethylchlorosilane (Aldrich) were used as received. Trimethylsilane was prepared by reduction of trimethylchlorosilane with lithium aluminum hydride (Aldrich), which was recrystallized from diethyl ether prior to use. LiN_3 was prepared using a published procedure, and its purity was determined by powder diffraction and IR spectroscopy.[24]

Preparation of $(HClGaN_3)_4$. Solid LiN_3 is added slowly through a solid addition funnel at 0 °C to a 30 mL benzene solution of Cl_2GaH (1.58 g, 13.1 mmol). After stirring for 12 h, the solvent is removed in a vacuum to yield a waxy solid at 85% yield. This material is extracted several times with hexane, and the combined filtrates are cooled at −5 °C to obtain a colorless crystalline solid. $HClGaN_3$ mp: 70 °C dec. Anal. Calcd: C, 0.0; H, 0.68; N, 28.4; Cl, 24.0; Ga, 47.02. Found: C, 0.20; H, 0.72; N, 28.06; Cl, 24.13; Ga, 47.00. IR (Nujol): 2112 (vs, $\nu_{as}(N_3)$) 1992 (s, ν_{as}(Ga−H)), 1363 (m), 1303 (m), 1243 (m, $\nu_{sym}(N_3)$), 668 (w), 668 (w), 668 (w), 575 (vs, ρ(Ga−H)), 406 (m, ν(Ga−N)), 334 (m). EIMS (*m/e*): 443 $[(HClGaN_3)_3^+ - H_2]$, 408 $[(HClGaN_3)_3^+ - HCl]$, 402 $[(HClGaN_3)_3^+ - HN_3]$, 261 $[(HClGaN_3)_2^+ - HCl]$.

Preparation of $(H_2GaN_3)_n$. A solution of H_2GaCl (0.435 g, 4.06 mmol) in benzene (25 mL) was added to a suspension of LiN_3 (0.260 g, 5.31 mmol) in toluene (20 mL). The mixture was stirred at ambient temperature for 3 h, during which time the suspension turned light gray. The mixture was then filtered, and the solvent was removed in a vacuum to yield a clear slightly viscous liquid. The filtrate (0.183 g) was readily identified as LiCl by powder X-ray diffraction. The product isolated in this fashion is stable at −30 °C, and minor decomposition is observed at room temperature. It is extremely difficult to collect, and any attempt to transfer the pure product from the reaction flask using a metal or glass spatula caused instant decomposition often accompanied with spontaneous ignition. The remaining residue is always crystalline GaN free of Cl or any other impurities. The sample used for CVD experiments was first dissolved in benzene and then transferred to the appropriate container. The solvent was removed in the vacuum line, and the sample was attached to the vacuum chamber. The gaseous precursor was transported into the reactor under vacuum through a leak valve. It is important to note that high-quality H_2GaCl must be used to synthesize H_2GaN_3. Halide contaminations such as $HGaCl_2$ in the starting material yielded impure products which were then treated with $LiGaH_4$ to remove the chloride impurity. Filtration gave a clear solution of H_2GaN_3 in toluene. **Caution:** Neat H_2GaN_3 is unstable in contact with sharp objects. It decomposes with release of heat and often ignites spontaneously. It should be handled with extreme care in solvents.

IR: 3360 (w, $\nu_{as}(N_3) + \nu_{sym}(N_3)$), 2470 (w, $2 \times \nu_{as}(N_3)$), 2130 (vs, $\nu_{as}(N_3)$) 1980 (s, ν_{as}(Ga−H)) 1240 ($\nu_{sym}(N_3)$), 672 (s, Ga−H, scissoring, twisting, wagging), 587 (m, ρ(Ga−H)), 479 (m, ν(Ga−H)), 345 (m, δ(M−N-M)). ^1H NMR: for 20 °C δ 4.87 (broad singlet, Ga−H); for −50 °C δ 4.81 (s, Ga−H), 4.71 (shoulder Ga−H). (The combination band at 3360 cm^{-1} should not be confused with an N−H stretch. We did not observe N−H type vibrational modes in the IR or N−H resonances in the NMR.) EIMS (*m/e*): 340 $[(H_2GaN_3)_3^+ - H_2]$, 300 $[(H_2GaN_3)_3^+ - N_3]$, 227 $[(H_2GaN_3)_2^+ - H]$, 186 $[(H_2GaN_3)_2^+ - N_3]$, 114 $(H_2GaN_3)^+$.

Structure of $[HClGaN_3]_4$. Air and moisture sensitive crystals were loaded into a 0.3 mm capillary and sealed under nitrogen. A suitable specimen was mounted vertically in a Siemens P4 autodiffractometer equipped with the LT-2a low-temperature devices preset at −100 °C. Centering of 25 randomly selected reflections between 15 and 30 2θ revealed a primitive tetragonal cell. Data collection of one-eighth of the hemisphere gave 3432 reflections that merged to 1628 unique reflections. The small absorption profile was corrected using ψ scan data collected at 10° intervals for four reflections with χ values near 90°. Solution by direct methods showed the asymmetric unit to be a cyclic tetramer of $[HClGaN_3]_4$ units with an alternating up−down Cl orientation. The intramolecular Ga−Ga distances ranged from 3.49 to 3.52 Å between azide-bridged Ga atoms and from 4.87 to 4.90 Å between transannular Ga−Ga distances. The tetramer units formed extended zigzag chains with an intermolecular Ga(3)−Ga(4) distance of 4.09 Å and a Ga(1)−Ga(2) distance of 4.18 Å. These intermolecular Ga−Ga interactions are bridged by chlorine atoms with the intermolecular Ga−Cl distances ranging from 3.53 to 3.74 Å. Convergence led to final $R/R_w = 0.0660/0.0605$. All data reduction, solution, and refinement calculations utilized the SHELTEXT Plus package of programs available from Siemens.

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Supporting Information Available: Listings of crystallographic experimental details, atomic coordinates, equivalent isotropic displacement coefficients, and complete bond distances and angles for non-hydrogen atoms (4 pages). See any current masthead page for ordering information and Web access instructions.

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