New Single-Source Precursor Approach to Gallium Nitride

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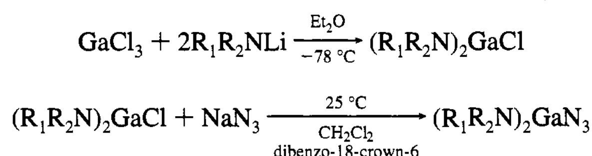
Gallium nitride (GaN) continues to generate significant interest for applications in high-luminosity light-emitting diodes and high-speed, high-power devices that are both radiation resistant and capable of operation at elevated temperatures.[1] In the context of metalorganic chemical vapor deposition (MOCVD) techniques, the most successful current approach to GaN involves the reaction of trimethylgallium or triethylgallium with ammonia at temperatures in excess of 900 °C.[2] Such elevated growth temperatures, however, result in thermal stresses in the cooling films as well as loss of stoichiometry due to nitrogen deficiency. While the use of alternate nitrogen[3] or gallium[4] sources has resulted in lower deposition temperatures, the deposited films are usually polycrystalline. It is only by the use of plasma-activated nitrogen in a molecular beam epitaxy (MBE)[5] or MOCVD[6] environment that the growth of epitaxial single crystalline films of GaN has been achieved at substrate temperatures less than 700 °C. We have devised a new class of single-source GaN precursor[7] that embodies labile amido substituents and an azide nitrogen source. One such precursor, $(Me_2N)_2GaN_3$ (**1**), has been examined in detail and found to deposit epitaxial single crystalline films of GaN at 580 °C.

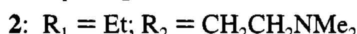
Solid **1** and liquids **2** and **3** were prepared in high yields by means of the two-stage procedure summarized below.



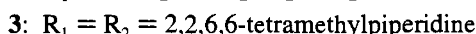
$$GaCl_3 + 2R_1R_2NLi \xrightarrow[-78\ °C]{Et_2O} (R_1R_2N)_2GaCl$$

$$(R_1R_2N)_2GaCl + NaN_3 \xrightarrow[CH_2Cl_2,\ dibenzo\text{-}18\text{-}crown\text{-}6]{25\ °C} (R_1R_2N)_2GaN_3$$

1: $R_1 = R_2 = Me$



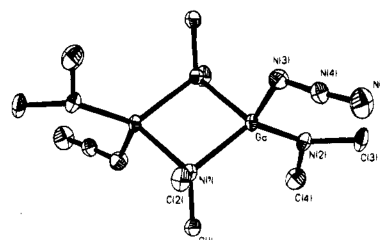
2: $R_1 = Et$; $R_2 = CH_2CH_2NMe_2$



3: $R_1 = R_2 =$ 2,2,6,6-tetramethylpiperidine

Analytical and spectroscopic data are in accord with the empirical formulas indicated above.[8] An X-ray crystallographic study of **1**[9] revealed that the solid state comprises a polymeric chain of dimeric units (Figure 1). The dimer is formed by means of two bridging dimethylamido (Me_2N) groups, and the resulting

(a)



(b)

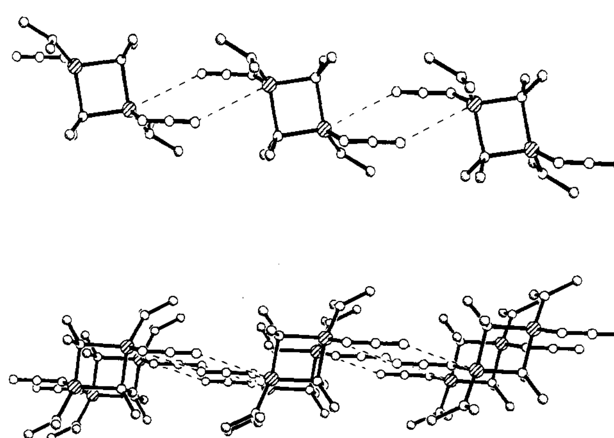


Figure 1. Molecular structure of bis(dimethylamido)gallium azide, $[(Me_2N)(N_3)Ga(\mu\text{-}NMe_2)]_2$ (**1**). (a) A view of the dimer of **1**. Selected bond distances (Å) and bond angles (deg) are as follows: Ga–N1 1.992(3), Ga–N1′ 1.998(3), Ga–N2 1.834(3), Ga–N3 1.919(4), Ga···Ga′ 2.8814(7), N1–C1 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(11), Ga–N1–Ga′ 92.48(11), N4–N3–Ga 124.8(3), N5–N4–N3 175.6(5). (b) The polymeric chain with hydrogen atoms omitted for clarity.

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(8) Compound **1**: mp 58–62 °C; ^1H NMR (300.15 MHz, C_6D_6) δ 2.30 (s, broad, 6H, NCH_3); $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6) 42.7 (s, NCH_3); MS (CI^+, isobutene, M = $C_8H_{25}N_{10}Ga_2$) 399.075 616 (399.077 528). **2**: bp 105 °C/10^{-2} Torr; ^1H NMR (300.15 MHz, C_6D_6) δ 2.67 (t, 2H, NCH_2), 2.59 (q, 2H, NCH_2CH_3), 2.38 (t, 2H, NCH_2), 2.14 (s, 6H, NCH_3), 0.98 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6) 58.6 (s, NCH_3), 50.1 (s, NCH_2), 46.4 (s, NCH_2), 46.0 (s, NCH_2), 12.4 (s, CH_2CH_3); MS (CI^+, isobutene, M = $C_8H_{25}N_{10}Ga_2$) 341.181 058 (341.181 850). **3**: bp 95 °C/10^{-2} Torr; ^1H NMR (300.15 MHz, C_6D_6) δ 1.53 (m, 4H, CH_2), 1.30 (s, 24H, CH_3), 1.23 (m, 8H, CH_2); $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6) 54.2 (s, $NC(CH_3)_2$), 40.2 (s, CH_2), 34.4 (s, $C(CH_3)_2$), 18.3 (s, CH_2); MS (CI^+, isobutene, M = $C_{18}H_{36}N_5Ga$) 391.221 937 (391.222 652).

(9) Crystal data for **1**: $C_4H_{12}N_5Ga$, M = 199.91, triclinic, $P\bar{1}$, a = 7.098(1) Å, b = 7.257(1) Å, c = 8.567(1) Å, α = 89.57(1)°, β = 78.74(1)°, γ = 74.51(1)°, V = 416.6(1) Å^3, ϱ = 1.594 mg/m^3, Z = 2, μ = 32.41 mm^{-1}, number of reflections used = 1960 (R_{int} = 0.0219) (2813 unique measured), R = 0.0375, R_w = 0.0472, Siemens P4 diffractometer, at −100 ± 1 °C, graphite monochromator, Mo Kα = 0.710 73 Å.

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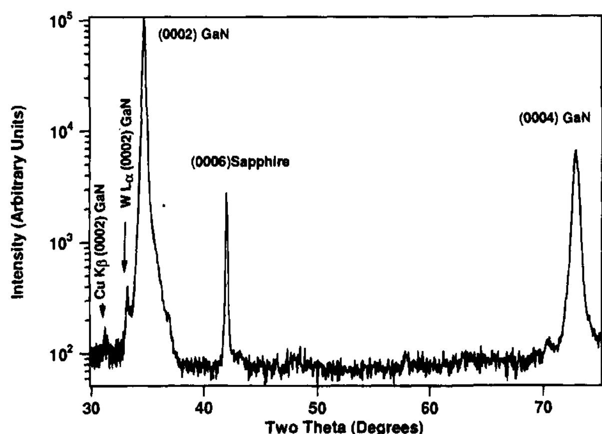

Figure 2. X-ray diffraction $\theta-2\theta$ scan of a GaN film grown with **1** at a substrate temperature of 580 °C.

Ga_2N_2 core is planar by virtue of its location on a crystallographic center of symmetry. The nonbridging positions are occupied by Me_2N and N_3 groups, and in turn, the polymeric chain is formed by dative interactions between the terminal nitrogen of each azide group and an adjacent gallium atom. Although the Ga−N distances for these interactions are long (3.431 Å), their effect is manifested in a marked distortion of the gallium geometry from tetrahedral toward trigonal bipyramidal. The shorter of the gallium−azide distances in **1** (1.919(4) Å) is indistinguishable from those in a bis(azide) of gallium (average 1.921(4) Å).[10] The metrical parameters for the bridging and terminal Me_2N groups are similar to those reported for $[(Me_2N)_2Ga(\mu\text{-}NMe_2)]_2$[11] and $[(Me_2N)(\mu\text{-}NMe_2)GaCl]_2$.[12]

A gas phase pyrolysis study of **1** was conducted in an apparatus described previously[13] at a pressure of 2×10^{-7} Torr (He carrier gas). Mass spectral monitoring of the peaks corresponding to $[(Me_2N)_2GaN_3]^+$, $[(Me_2N)_2Ga]^+$, and $[Me_2NGa]^+$ in the effluent vapor indicated that the thermal decomposition of **1** commenced at 250 °C. Moreover, since the decay of the foregoing peaks was accompanied by an increase in intensity of the $[Me_2N]^+$ peak, the initial thermolytic step is evidently cleavage of the $Ga-NMe_2$ bond.

Film growth experiments were carried out in a chemical beam epitaxy reactor[13] in the temperature range 250−620 °C. Compound **1** was sublimed into the reactor from a heated saturator at 82 °C, and the pressure during growth was 10^{-4}−10^{-5} Torr. The resistively heated (100) GaAs and (0001) sapphire substrates were glued with indium onto a tantalum stage. In agreement with the thermolysis results, it was found that GaN film growth (on (0001) sapphire) could be achieved at a temperature as low as 250 °C. Despite the amorphous nature of these films, they exhibited the correct band gap for GaN (3.4 eV). Epitaxial growth of GaN on (0001) sapphire was achieved by employing higher deposition temperatures. The $\theta-2\theta$ X-ray diffraction (XRD) scan of GaN deposited at 460 °C revealed the persistance of slight polycrystallinity. However, by 580 °C these additional features had disappeared, leaving only the peaks at 2θ of 34.6° and 73° which could correspond to either the wurtzitic ((0002) and (0004) planes, respectively) or the cubic ((111) or (222) planes, respectively) phases of GaN. This question was resolved by means of a χ scan, which revealed that the phase is wurzitic. Further confirmation of epitaxial single crystalline growth was provided by pole figure analysis of a 0.7 μm thick film. The full width at half maximum of the 2θ peak at 34.6° was ~12 $arcmin^{-1}$.

When the substrate was changed to (100) GaAs, polycrystalline growth was observed at 500 °C as evidenced by the appearance of XRD peaks at 34.6° ((111) or (0002) plane) and 40.1° ((002) plane). Ramping the deposition temperature to 620 °C (the limit of GaAs stability) resulted in an increase of intensity of the 40.1° peak at the expense of the 34.6° peak, thus suggesting the approach to epitaxial growth to cubic GaN. SEM examination of GaN film growth on (0001) sapphire at 580 °C indicated a smooth, crack-free morphology with an absence of surface features up to a magnification of 48000×. The stoichiometric nature of the films was confirmed by X-ray photoelectron spectroscopy. Using GaAs implanted standards, a noncalibrated SIMS (secondary ion mass spectroscopy) analysis of the epitaxial film grown at 580 °C resulted in estimated oxygen and carbon contents of 5×10^{20} atoms/cm^3 and 2×10^{21} atoms/cm^3, respectively.

In summary, a new class of GaN single-source precursors has been developed which feature labile amido leaving groups and an azide nitrogen delivering moiety. One of these precursors was used to deposit epitaxial GaN at 580 °C.

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Supplementary Material Available: Experimental details for the synthesis of **1**−**3** and atomic coordinates, thermal parameters, bond distances, bond angles for **1** (7 pp); observed and calculated structure factors for **1** (5 pp). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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