

GaN Film Growth Using Single-Source Precursors

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Use of the single-source precursor dimethylgallium azide in the growth of GaN films has been explored. Thin polycrystalline films with strong (0002) preferred orientation were deposited over the temperature range 450–650 °C and the pressure range 2×10^{-5} – 3×10^{-4} Torr on (100) GaAs, (111) GaAs, (0001) sapphire, and quartz. Films deposited at the lower temperature (475 °C) were found to have a bandgap of approximately 3.3 eV. At higher temperatures the films were darker and cracks were evident on the surface. This darkening effect can be partially suppressed by the simultaneous use of dimethylhydrazine. The effect of GaN buffer layers deposited at low temperature prior to high-temperature film growth has been explored. An activation energy of 15 kcal/mol has been calculated for the deposition reaction. An increase in the precursor partial pressure was found to increase the growth rate sharply. GaN growth was also attempted from dimethylhydrazodimethylgallium; the resultant films were found to be polycrystalline, possessing poor surface morphology.

Introduction

The III–V nitrides are receiving increased interest for several semiconductor applications due to their desirable properties.^{1–8} The semiconductor GaN is one of the three nitrides, including AlN and InN, that form a continuous alloy of direct bandgap semiconductor that ranges from 1.9 to 6.2 eV. They offer the potential of forming optoelectronic devices that can operate in the wavelength range from the infrared to the ultraviolet.⁹ GaN because of its wide bandgap, 3.4 eV, and high thermal conductivity, 1.5 W cm^{-1} , has potential for application in high-speed, high-power devices that can operate at high temperature and are radiation resistant.⁴ It is also being considered as an insulation or passivation layer on GaAs.¹⁰

Several approaches for the growth of GaN have been studied. The high equilibrium pressure of nitrogen at the crystal growth temperatures makes the growth of bulk GaN crystals difficult.¹¹ Film growth has been conducted primarily by chloride vapor-phase epitaxy,

using gallium chloride and ammonia,¹² and by organo-metallic vapor-phase epitaxy, using trimethylgallium or triethylgallium and ammonia.^{13–20} Most of these techniques require high temperatures (>800 °C) to decompose NH_3 . These films typically have a high-background n-type carrier concentration, which is believed to be due to nitrogen vacancies arising from the high nitrogen vapor pressure of GaN under the growth conditions.^{21–24} High substrate temperature also results in residual strain that arises during cooling due to thermal and lattice mismatch. Gas source molecular beam epitaxy (MBE), using a gallium beam has been able to lower the deposition temperature, though the material grown still has a high n-type background.²⁵ Plasma excitation of nitrogen in a MBE environment has also been investigated.^{26,27} Alternative sources of nitrogen, including hydrazine (N_2H_4) and dimethylhydrazine ($\text{Me}_2\text{N}_2\text{H}_2$), have also been investigated.^{28–30}

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Single-source precursors, with a preformed Ga-N bond, have been used for the growth of GaN films at low temperature. By variation of the gallium and nitrogen substituents, the reactivities of these precursors can be significantly altered. GaN film growth has been attempted using the single-source precursors triethylgallium monamine, $\text{Et}_3\text{Ga}\cdot\text{NH}_3$, and diethylgallium azide, $[\text{Et}_2\text{GaN}_3]_n$.^{31,32} $\text{Et}_3\text{Ga}\cdot\text{NH}_3$ decomposed in the bubbler to form diethylgallium amide, Et_2GaNH_2 , which further decomposed in the bubbler resulting in a reduction in vapor pressure and growth rate.³¹ Films grown from $[\text{Et}_2\text{GaN}_3]_3$ at 350 °C had low growth rates (15 Å/min) and those deposited at higher temperatures had high impurity concentrations ($C \sim 10\%$).³² Ho et al. also observed low growth rates (<17 Å/min) with $[\text{Et}_2\text{GaN}_3]_3$.³³ Addition of NH_3 increased the growth rates, but at temperatures in excess of 600 °C the growth rates dropped again presumably due to gas-phase depletion. Hexakis(dimethylamido)digallium, $\text{Ga}_2(\text{NMe}_2)_6$, and NH_3 have been used to deposit polycrystalline GaN at 200 °C.³⁴

We report film growth with dimethylgallium azide ($[\text{Me}_2\text{GaN}_3]_n$) and dimethylhydrazidodimethylgallium ($(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$) to assess the feasibility of these single source GaN precursors. The azide (N_3) ligand was selected because azides have a tendency to eliminate N_2 leaving a nitrogen atom bonded to gallium.^{35,36} The methyl ligand was chosen to keep the molecular weight low and to provide high vapor pressure, which is believed to be crucial in ensuring intact transportation of the precursor to the growth surface. $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ was designed with no Ga-N-C bond and contains the NMe_2 substituent, which was expected to eliminate as dimethylamine (HNMe_2) or trimethylamine (NMe_3). Film growth was conducted at reduced pressure (ca. 1×10^{-5} Torr) as it has been observed that GaAs crystalline quality improved at lower pressure when using single-source precursors.^{37,38}

Methods

$[\text{Me}_2\text{GaN}_3]_n$ was prepared by the reaction of Me_2GaCl with NaN_3 ; further details on its synthesis and structure are available in literature.³⁹ Electronic grade reagents and grease-free glassware were used wherever possible in its synthesis. $[\text{Me}_2\text{GaN}_3]_n$ has a vapor pressure of 0.05 Torr at 55 °C.⁴⁰ $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ was prepared by reacting (LiNHMe_2) with Me_2GaCl ; complete details on synthesis and structure are to be reported soon.^{41,42}

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The apparatus used for the gas-phase pyrolysis studies and the reactor used for film growth have been described elsewhere.^{37,43} Only significant features have been described herein. For pyrolysis the precursor was loaded in a leak-free stainless steel assembly to prevent exposure to atmosphere. This assembly was placed in an oven where it was typically heated to 60 °C. During pyrolysis the sublimed precursor was swept by helium carrier gas into a quartz tube. The tube temperature was increased at a fixed rate (1 °C/s), and the decomposition products were analyzed by a mass spectrometer. Between experiments the pyrolysis apparatus was maintained at 2×10^{-7} Torr by a diffusion pump and mass spectral analysis indicated the residual gases were H_2O , CO , and hydrocarbons.

For film growth, the precursor was again placed in a saturator that was heated in an oven typically to 60 °C for $[\text{Me}_2\text{GaN}_3]_n$ or 40 °C for $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$. Lines downstream of the saturator were either heated by the oven or by heating tapes to prevent condensation of the sublimed precursor. During growth the sublimed precursor was swept by helium carrier gas into a stainless steel cross where the substrate was located. The growth reactor was maintained at less than 1×10^{-8} Torr (the ion gauge limit) by a turbomolecular pump. The deposition chamber was equipped with a mass spectrometer to ensure that conditions remained steady throughout each film growth experiment. Mass spectral analysis indicated the residual gases in the growth chamber to be H_2O , CO , CO_2 , and hydrocarbons.

In the growth chamber, the substrate was glued with indium onto a tantalum foil and placed on a tantalum stage. A portion of the substrate was masked by tantalum foil to determine the thickness of the deposited film. The substrate was resistively heated, and the temperature was measured by a thermocouple spot welded to the tantalum foil. The stage was loaded through a load lock section. After the load lock was pumped down to 1×10^{-7} Torr, the substrate was transferred to the deposition chamber. GaAs substrates were solvent cleaned prior to loading in the reactor. They were pretreated by heating to 600 °C in the deposition chamber for ca. 5 min prior to film growth to flash off the native oxide.⁴⁴ Growth was also conducted on (0001) sapphire and quartz substrates that were solvent cleaned prior to loading in the reactor. Growth was conducted using $[\text{Me}_2\text{GaN}_3]_n$ over the temperature range 450–650 °C and the pressure range 2×10^{-5} – 3×10^{-4} Torr. Simultaneous use of $\text{Me}_2\text{N}_2\text{H}_2$ along with $[\text{Me}_2\text{GaN}_3]_n$ for GaN was also explored.⁴⁵ Growth was also conducted using $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ over the temperature range 525–640 °C and the pressure range 2×10^{-5} – 1×10^{-4} Torr.

After growth, the film was removed from the reactor and examined by X-ray diffraction using a single-crystal monochromator ($\text{Cu K}\alpha$ radiation was used), scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (IR) spectroscopy. Optical properties were measured by light-transmission studies. The effect of temperature and pressure on growth rate was determined by measuring the height of the step created by the tantalum mask with a profilometer.

Results and Discussion

Pyrolysis studies were conducted to determine the minimum film growth temperature and to determine

(40) The compound was loaded in a saturator and attached to a baratron gauge. The entire assembly was placed in an isothermal oven and was pumped by a diffusion pump. The diffusion pump was isolated from the rest of the assembly during vapor pressure measurements, which were done using the static method.

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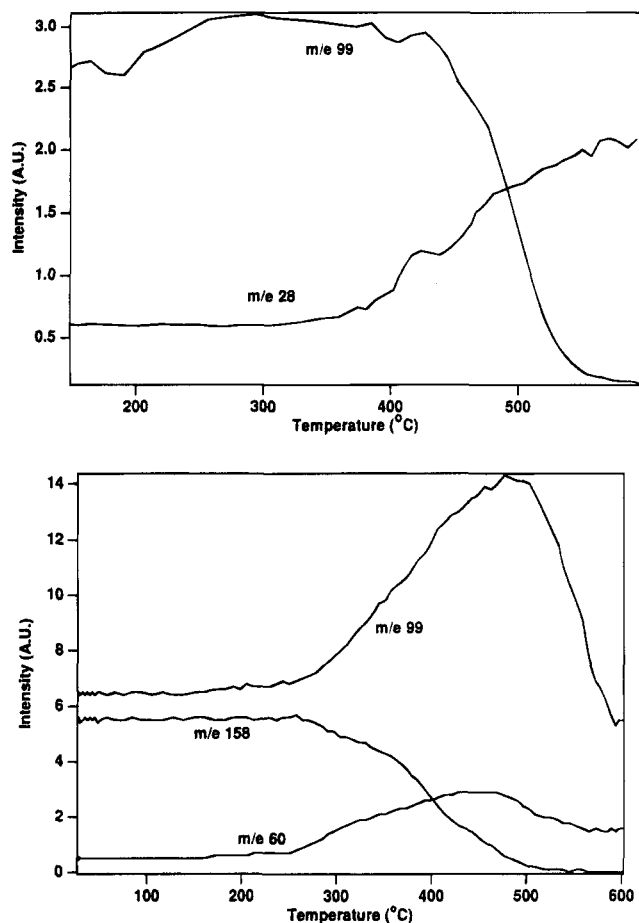


Figure 1. (a, top) Fragment m/e 99 (Me_2Ga) and m/e 28 (N_2) signals plotted as a function of temperature during the pyrolysis of $[\text{Me}_2\text{GaN}_3]_n$. (b, bottom) Fragment m/e 158 ($\text{Me}_2\text{-GaNH}(\text{NMe}_2)$), m/e 99 (Me_2Ga), and m/e 60 ($\text{NH}(\text{NMe}_2)$) signals plotted as a function of temperature during the pyrolysis of $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$.

whether the Ga–N bond cleaves before ligand loss. They are not indicative of the reaction mechanism occurring on the surface during film growth. The pyrolysis results for $[\text{Me}_2\text{GaN}_3]_n$ are summarized in Figure 1a. The m/e 99 fragment (Me_2Ga) is an indicator of the parent molecule. Peaks corresponding to Ga (69, 71) and MeGa (84, 86) were also observed. The intensity of the m/e 28 signal (N_2) starts increasing at 375 °C (Figure 1a) indicating that the azide ligand decomposes at that temperature forming N_2 . The intensity of the m/e 99 signal starts decreasing at 425 °C and is believed to be due to the cleavage of the methyl–gallium bond as pyrolysis of Me_3Ga shows similar behavior.⁴⁶ To ensure removal of the methyl ligand from $[\text{Me}_2\text{GaN}_3]_n$ the minimum film growth temperature was 450 °C.

Pyrolysis results of $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ have been summarized in Figure 1b. The m/e 158 signal, corresponding to the monomer $\text{Me}_2\text{GaNH}(\text{NMe}_2)$, is found to decrease at 260 °C, indicating that the precursor starts to decompose at that temperature. It is accompanied by a concomitant decrease in the m/e 59 signal, $\text{NH}(\text{NMe}_2)$ (not shown) and an increase in the m/e 60 signal ($\text{NH}_2(\text{NMe}_2)$). The m/e 99 (Me_2Ga) signal increases at 260 °C as well indicating that the methylgallium bonds remain intact. This suggests that the precursor decom-

(46) Unpublished results.

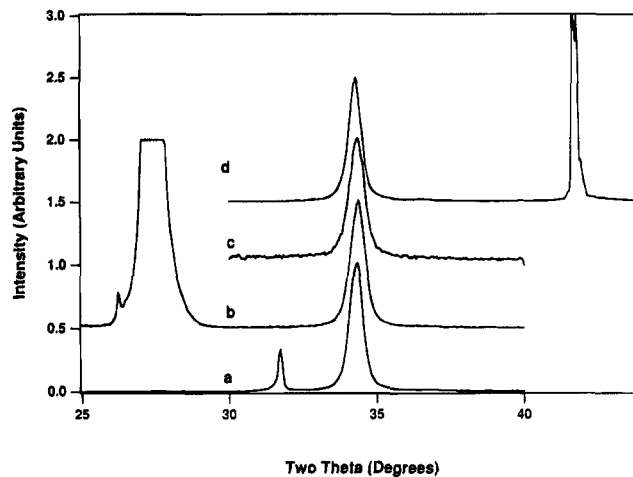


Figure 2. X-ray diffraction of GaN films grown from $[\text{Me}_2\text{-GaN}_3]_n$ on (a) (100) GaAs; (b) (111) GaAs; (c) quartz; (d) (0001) sapphire. The peaks seen are 31.6°, (100) GaAs; 34.6°, (0002) GaN; 27.3°, (111) GaAs; 41.7°, (0006) sapphire.

poses by cleavage of the Ga–N bond at 260 °C forming $\text{NH}(\text{NMe}_2)$ and a volatile fragment bearing Me_2Ga . $\text{NH}_2(\text{NMe}_2)$ is the primary pyrolysis reaction product formed by abstraction of a H atom from the pyrolysis tube walls by $\text{NH}(\text{NMe}_2)$. The identity of the molecule that forms in the pyrolysis tube from Me_2Ga is unknown, but it has a higher electron impact ionization efficiency for the m/e 99 signal than the original precursor, $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$. The fragment m/e 99 decreases at 500 °C, and this is attributed to the cleavage of the Ga–C bond. Film growth from the precursor $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ was conducted at temperatures in excess of 500 °C.

The X-ray diffraction pattern of a 5.8 μm GaN film deposited from $[\text{Me}_2\text{GaN}_3]_n$ on (100) GaAs at 600 °C and 1×10^{-4} Torr is shown in Figure 2a. The peak at 2θ of 34.6° is likely the (0002) GaN peak indicating a wurtzitic film. A weak (0004) peak was also observed at 73°. The lack of other peaks indicates that the film is highly oriented or textured with the (0002) planes parallel to the growth surface. Growth of GaN on (100) GaAs has typically resulted in a zinc blende structure.^{47,48} This interesting feature of the film growth may be related to the precursor structure and the preexisting bond between gallium and nitrogen, which may stay intact during the deposition process.

Films deposited on (111) GaAs, (0001) sapphire, and amorphous quartz using $[\text{Me}_2\text{GaN}_3]_n$ also had the highly oriented wurtzitic structure (Figure 2). No other GaN diffraction peaks were observed. This indicates that the crystalline quality of the deposited films over the conditions investigated was influenced by the precursor and was independent of the template provided by the substrate. Different growth conditions could result in a greater substrate influence and single crystalline films. The full width at half-maximum (fwhm) of the (0002) GaN peak was approximately 30 arc min. Poor crystallinity and residual stresses in the film can contribute to a broad X-ray peak.^{49,50} The cracking of

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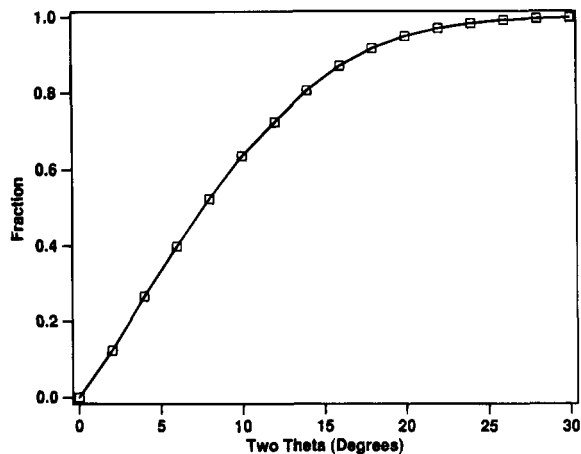


Figure 3. Partial pole figure analysis of a 3.2 μm thick GaN film deposited from $[\text{Me}_2\text{GaN}_3]_n$ on (100) GaAs at 570 $^\circ\text{C}$ and 8×10^{-5} Torr.

Table 1. Full Widths at Half-Maxima of (0002) GaN X-ray Diffraction Peak Grown from $[\text{Me}_2\text{GaN}_3]_n$ on Various Substrates

substrate		GaN fwhm (arc min)	temp ($^\circ\text{C}$)	pressure (Torr)
type	fwhm (arc min)			
(100) GaAs	4.4	30	620	7×10^{-5}
(111) GaAs	8.7	32	550	8×10^{-5}
(0001) sapphire	4.2	30	620	6.5×10^{-5}
quartz		48	550	8×10^{-5}

the films (discussed later) suggests that the films are under high stress. Moustakas et al. have observed GaN fwhm to depend on the substrate orientation, ranging from 10 to 38 arc min.⁵¹ Amano et al. have obtained lower fwhm (~ 3 arc min) by using an AlN buffer layer.⁵² Table 1 gives the fwhm of (0002) GaN peak and the substrate peak for the various substrates studied. The large values of the fwhm for the substrate are probably due to the heterochromatic nature of the incident X-rays and incomplete absorption by the filter of radiations other than Cu K α . Using a better diffractometer could potentially result in lower fwhm's for both the films and the substrates.

To determine whether the GaN film was single crystal or simply highly oriented, a 3.2 μm thick film, deposited at 570 $^\circ\text{C}$ and 8×10^{-5} Torr on (100) GaAs was examined by pole figure analysis and partial pole figure analysis, which measures the density of poles (crystallographic directions) for the various planes in the crystal. The pole figure analysis revealed a maximum in the (0002) diffracted peak at 7 $^\circ$ from the normal to the growth surface, indicating that the (0002) planes are not parallel to the growth surface. This was further confirmed by partial pole figure analysis, which revealed that 95% of the (0002) planes are within 20 $^\circ$ of the (100) GaAs plane. The partial pole figure results shown in Figure 3 indicate that the film has a strong preferred orientation but is not single crystalline. The highly textured nature of the film might result in a reduced X-ray intensity of the other planes accounting for their

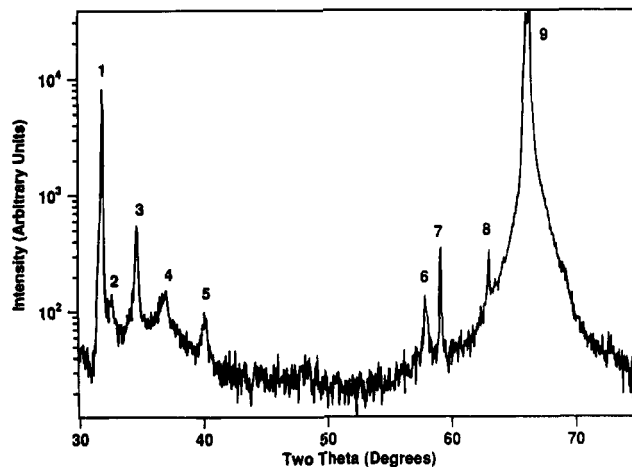


Figure 4. X-ray diffraction of a 3.65 μm thick GaN film grown from $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ on (100) GaAs at 580 $^\circ\text{C}$ and 1×10^{-4} Torr. The diffraction peaks seen are (1) 31.6 $^\circ$, (002) GaAs; (2) 32.4 $^\circ$ (1010) GaN; (3) 34.6 $^\circ$, (0002) GaN; (4) 36.7 $^\circ$, (1011) GaN; (5) 40 $^\circ$, (100) GaN; (6) 57.9 $^\circ$, (1120) GaN; (7) 59 $^\circ$, Cu K β (004) GaAs; (8) 63.6 $^\circ$, WL α (004) GaAs; (9) 66.05 $^\circ$, (004) GaAs.

absence in the θ -2 θ diffraction scan. Kouvetakis et al. have observed polycrystalline GaN growth using $[\text{Et}_2\text{GaN}_3]_3$ at 350 $^\circ\text{C}$ and 2 Torr on Si substrates.³² Ho et al. also observed polycrystalline growth while using $[\text{Et}_2\text{GaN}_3]_3$ and NH_3 on (100) Si but highly textured growth was seen on (0001) sapphire at 5 Torr and higher temperatures (> 600 $^\circ\text{C}$).³³

The effect of substrate preparation on film texture was studied by conducting film growth with $[\text{Me}_2\text{GaN}_3]_n$ in a MBE environment.⁵³ A (100) GaAs substrate was pretreated by standard MBE techniques, and surface cleanliness was established by reflection high-energy electron diffraction. A 1 μm thick film was deposited at 600 $^\circ\text{C}$ and examined by X-ray diffraction. The film showed a strong (0002) orientation, indicating that impurities at the growth surface are not the cause of the orientation.

To understand the significance of nitrogen substituents on the film quality, growth was also conducted using $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$. Figure 4 shows the double-crystal X-ray diffraction spectrum of a 3.65 μm thick GaN film deposited on (100) GaAs at 580 $^\circ\text{C}$ and 1×10^{-4} Torr. A film deposited with $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ on (111) GaAs was also polycrystalline. While the film grown from $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ retains the wurtzitic nature they are not as highly textured as films grown from $[\text{Me}_2\text{GaN}_3]_n$. Poor film quality might be related to cleavage of the Ga-N bond at 260 $^\circ\text{C}$.

Among other factors the (0002) texture of the GaN films grown from $[\text{Me}_2\text{GaN}_3]_n$ is dependent on the nitrogen ligand structure. The wurtzitic nature of the films may also be determined by the preexisting Ga-N bond. GaN growth using conventional precursors such as Me_3Ga and NH_3 at such low temperatures typically results in films that are either amorphous or have a very small degree of crystallinity.^{24,54,55} These low-temperature films are often used as buffer layers for epitaxial growth.

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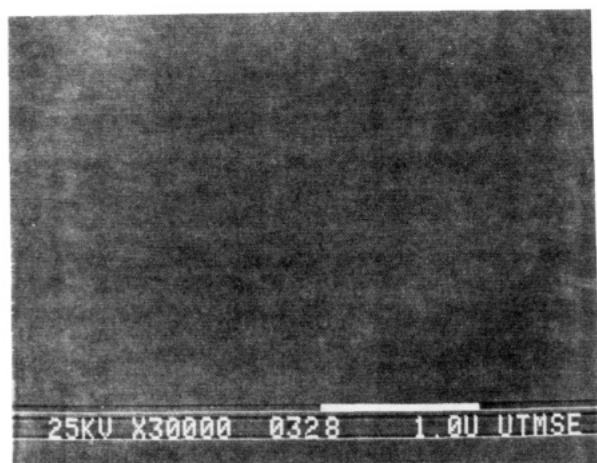
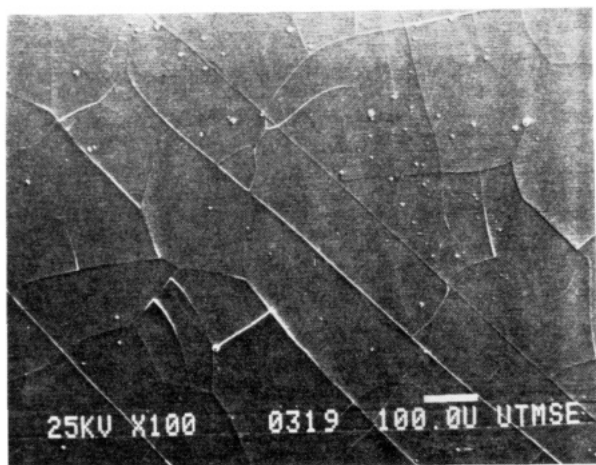


Figure 5. (a, top) Low-magnification SEM photograph of a GaN film grown from $[\text{Me}_2\text{GaN}_3]_n$ at 600 °C and 1×10^{-4} Torr on (100) GaAs. (b, bottom) High-magnification SEM photograph of a GaN film grown from $[\text{Me}_2\text{GaN}_3]_n$ at 600 °C and 8×10^{-5} Torr on (100) GaAs.

Thin films ($<0.8 \mu\text{m}$) deposited at low temperature ($<525 \text{ °C}$) on the transparent sapphire substrate were visually observed to have a predominantly yellowish appearance. The thicker films deposited at the higher temperatures were observed to have a darker appearance, and cracks could clearly be seen on them. Films deposited on GaAs also had a similar darkening trend. Chu observed a similar film darkening with increasing temperature, which he attributed to an increase in the gallium content of the films.⁵⁶

The morphology of the films grown from $[\text{Me}_2\text{GaN}_3]_n$ was examined in a SEM. Figure 5a shows a film deposited on GaAs at 600 °C. The cracks may be due to thermal and lattice mismatch with the substrate or unintentional impurities in the film. Similar cracking have been observed by Ito et al.⁵⁷ While the cause of the darkening and cracking is not certain, possible explanations are an increase in impurity incorporation or an altered Ga/N ratio. At high magnification ($>30\,000\times$) these films showed no other surface features as shown in Figure 5b. To study the nature of the film at the substrate interface, a film grown from $[\text{Me}_2\text{GaN}_3]_n$ was separated from the substrate and then

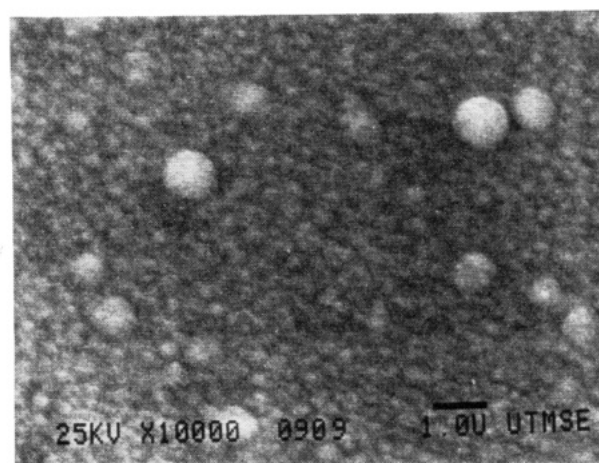
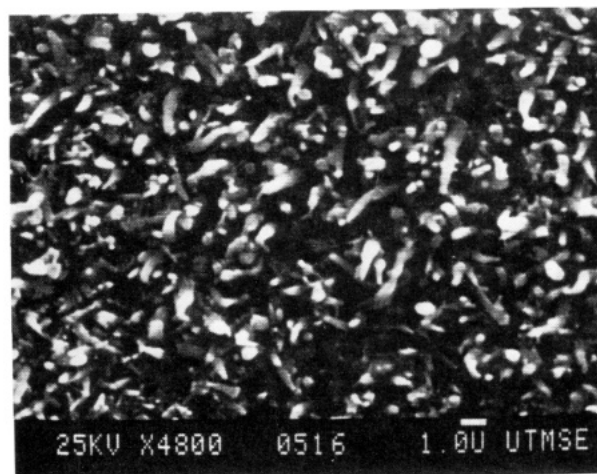


Figure 6. (a, top) SEM photograph of a GaN film grown from $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ at 580 °C and 1×10^{-4} Torr on (100) GaAs. (b, bottom) SEM photograph of a GaN film grown from $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ at 530 °C and 1×10^{-4} Torr on (111) GaAs.

examined by SEM. For mechanical integrity the GaN film was glued to quartz and the substrate was then removed by etching.⁵⁸ The exposed film face was found to be cracked indicating that the cracks propagate to/from the interface.

A SEM photograph of a film deposited from $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ at 580 °C and 1×10^{-4} Torr on (100) GaAs is shown in Figure 6a. The film has the appearance of precipitated particles, which suggests poor adhesion to the substrate. Again, the poor morphology is believed to be related to the Ga–N bond cleavage. Film growth with the same precursor on (111) GaAs showed improved morphology (Figure 6b), indicating that substrate orientation affects film morphology. From the above study it can be concluded that the morphology is influenced by the precursor, substrate, and the growth temperature. Due to the poor morphology and polycrystallinity of the films grown with $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$, this precursor was not studied further.

Recently, the use of buffer layers of AlN or GaN have been reported to improve the GaN film quality.^{24,56,59,60} A thin yellowish GaN buffer layer (ca. $0.1 \mu\text{m}$) was

(58) The etching solution used was 8:1:1 $\text{H}_2\text{O}_2:\text{H}_2\text{O}:\text{H}_2\text{SO}_4$.

(59) Yoshida, S.; Misawa, S.; Gonda, S. *Appl. Phys. Lett.* **1983**, *42*, 427.

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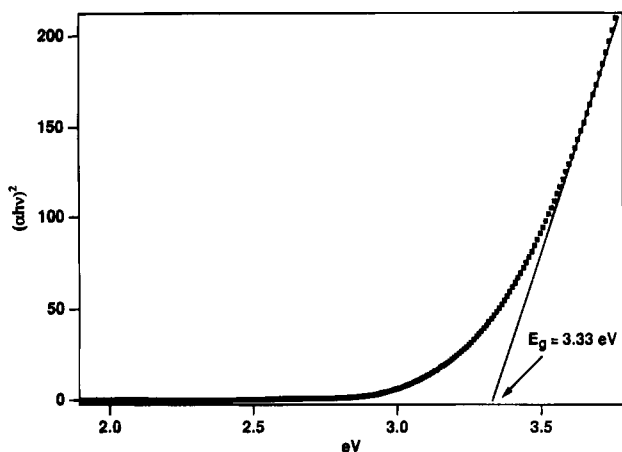


Figure 7. Absorbance of a GaN film deposited on (0001) sapphire from $[\text{Me}_2\text{GaN}_3]_n$ at 475°C and 3×10^{-4} Torr as a function of the photon energy.

Table 2. Effect of Growth Temperature and Precursors on the Bandgap

temp ($^\circ\text{C}$)	precursor used	bandgap (eV)
475	$[\text{Me}_2\text{GaN}_3]_n$	3.3
525	$[\text{Me}_2\text{GaN}_3]_n$	2.5
625	$[\text{Me}_2\text{GaN}_3]_n$	2.0
540	$[\text{Me}_2\text{GaN}_3]_n + \text{Me}_2\text{N}_2\text{H}_2$	2.75

deposited using $[\text{Me}_2\text{GaN}_3]_n$ on a (0001) sapphire substrate at 490°C . The substrate was remounted with a portion of the buffer layer being covered by the tantalum mask. A $2.65\ \mu\text{m}$ thick GaN film was deposited at 625°C over the buffer layer. The deposited film was found to be dark, cracked, and not very adherent, indicating that the buffer layer was not very effective in reducing stress and improving morphology. However, the masked buffer layer did not deteriorate in quality, implying that the low-temperature films are robust and can withstand exposure to high temperature.

The optical and electrical properties of the films were measured. Hall measurements attempted on the uncracked GaN films grown from $[\text{Me}_2\text{GaN}_3]_n$ indicated a very high resistivity ($>300\ \Omega\ \text{cm}$). This could be due to a high level of unintentional impurities, lattice irregularities, or nonstoichiometry in the film. Carbon (determined by SIMS) may be the cause of the high resistivity.⁹

Transmission measurements were conducted on GaN films grown on sapphire. Figure 7 shows the bandgap of a film deposited from $[\text{Me}_2\text{GaN}_3]_n$ at low temperature (475°C) as 3.33 eV, which compares favorably with the theoretical value of 3.4 eV. With an increase in growth temperature the measured bandgap was found to decrease, and the trend is tabulated in Table 2. The apparent decrease in the bandgap measured by transmission spectroscopy with increasing growth temperature could be due to nitrogen deficiency or impurity incorporation in the films at the higher temperatures. SIMS measurements of a GaN film grown on GaAs at 600°C using GaAs implanted standards showed an O concentration of $1 \times 10^{20}\ \text{cm}^{-3}$ and the C signal saturated the detector. The source of the C impurity is believed to be the methyl ligands on the gallium, while the source of the O impurity could be impurities present in either the precursor or film growth chamber. Growth of GaN was conducted at 540°C using $\text{Me}_2\text{N}_2\text{H}_2$ and $[\text{Me}_2\text{GaN}_3]_n$. $\text{Me}_2\text{N}_2\text{H}_2$ has been used as a N source in

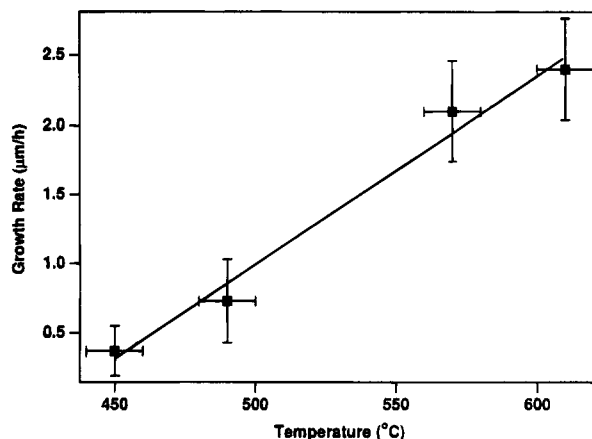


Figure 8. Effect of temperature on GaN growth rate on (100) GaAs at 8×10^{-5} Torr using $[\text{Me}_2\text{GaN}_3]_n$.

GaN film growth by Okumura.⁴⁷ Furthermore, we expected lower C incorporation since growth of GaAs using tris-dimethylaminoarsine, $(\text{Me}_2\text{N})_3\text{As}$, along with Me_3Ga resulted in significantly reduced C incorporation than growth with AsH_3 and Me_3Ga suggesting that the Me_2N ligand helps in removing C from the surface.⁶¹ The resulting film was not as dark as a GaN film grown from $[\text{Me}_2\text{GaN}_3]_n$ at 525°C and no cracks were observed on its surface. It also had a higher bandgap as shown in Table 2, indicating that the film was of better quality. The improvement in film quality could be due to better Ga/N stoichiometry or to reduced C incorporation.

XPS measurements of the Ga/N ratio and the O and C concentrations were attempted on films grown with $[\text{Me}_2\text{GaN}_3]_n$. Oxygen and carbon peaks were found only at the surface and disappeared upon sputtering ca. 100 Å of the film. This is believed to be from exposure to the ambient while transferring the film from the film growth apparatus to the XPS apparatus. Carin et al., who have studied GaN by XPS, have observed similar results.⁶² Since the sputtering process alters the Ga/N stoichiometry in the film, the measured values are not true indicators of the film stoichiometry but can be used for relative comparison of different films. The measured Ga/N ratio increased slightly with increasing temperature but decreased with the use of $\text{Me}_2\text{N}_2\text{H}_2$ as a source of additional nitrogen. Since no C signal could be detected in the bulk of the film, the effect of temperature on C incorporation could not be studied. Some films were found to have a bluish glow when irradiated by X-rays, as would be expected of a GaN film.

The effect of substrate temperature on growth rate of GaN from $[\text{Me}_2\text{GaN}_3]_n$ is plotted in Figure 8. The growth rate was found to increase with an increase in temperature, suggesting that the surface reaction rate is important over the entire range of temperatures studied. The activation energy for the deposition reaction was calculated to be 15 kcal/mol. The effect of pressure on growth rate is illustrated in Figure 9. The growth rate increases with an increase in the partial pressure of $[\text{Me}_2\text{GaN}_3]_n$, indicating that the rate of delivery of the precursor to the substrate also determines the growth rate.

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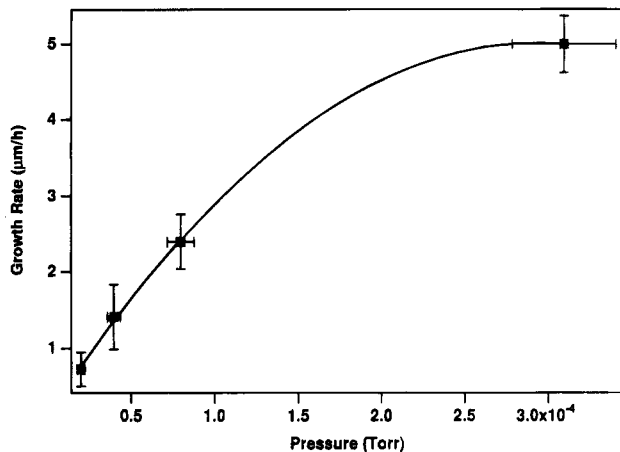


Figure 9. Effect of partial pressure on GaN growth rate on (100) GaAs at 615 °C using $[\text{Me}_2\text{GaN}_3]_n$.

In contrast to film growth with $[\text{Et}_2\text{GaN}_3]_3$, which had a high hydrogen content that may have led to the air sensitivity problems ($\text{O} > 20\%$ upon exposure to ambient),³² films grown from $[\text{Me}_2\text{GaN}_3]_n$ did not display any Ga-H IR stretches and do not appear to be as air sensitive. The growth rates observed with $[\text{Me}_2\text{GaN}_3]_n$ are significantly higher than those seen with $[\text{Et}_2\text{GaN}_3]_3$. Ho et al. observed a reduction in growth rate with $[\text{Et}_2\text{GaN}_3]_3$ at temperatures in excess of 600 °C.³³ Over the entire range of temperature studied, no reduction in growth rate was observed with $[\text{Me}_2\text{GaN}_3]_n$.

This could be due to a lack of gas-phase reactions because of the low pressure used for growth. Gas-phase depletions were believed to be the cause of the reduced growth rates at the higher temperatures with $[\text{Et}_2\text{GaN}_3]_3$.

In summary, GaN films have been grown from $[\text{Me}_2\text{GaN}_3]_n$ and $(\text{Me}_2\text{GaNH}(\text{NMe}_2))_2$ at low temperature and pressure. Pyrolysis studies have been conducted to determine the ligand loss temperature and understand the decomposition pathway. The films deposited from $[\text{Me}_2\text{GaN}_3]_n$ were found to have a highly textured nature and a smooth morphology in spite of the macroscopic cracks present on them. Simultaneous dosing of $\text{Me}_2\text{N}_2\text{H}_2$ has been found to eliminate the cracking and improve the film quality. A low-temperature gallium nitride buffer layer did not significantly reduce the cracked nature of the film. The deposition rate was found to increase with an increase in either the deposition temperature or precursor partial pressure.

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