

GALLIUM NITRIDE GROWTH USING DIETHYLGALLIUM CHLORIDE AS AN ALTERNATIVE GALLIUM SOURCE

Ling Zhang,* Rong Zhang,* Marek P. Boleslawski,** T.F. Kuech*

*Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706.

**Aldrich Chemical, Milwaukee, WI.

Cite this article as: MRS Internet J. Nitriden Semicond. Res. 4S1, G3.62 (1999).

ABSTRACT

Metal organic vapor phase epitaxy (MOVPE) of GaN has been carried out using diethyl gallium chloride (DEGaCl) and ammonia. The growth rate and efficiency of the DEGaCl-based growth decreases with increasing temperature when compared to trimethyl gallium (TMG)-based growth under similar conditions. Both low temperature buffer and the high temperature GaN layers were grown using the DEGaCl-NH₃ precursor combination on the basal plane of sapphire and compared to similar structures grown using TMG and NH₃. DEGaCl-based growth reveals an improved growth behavior under identical growth conditions to the conventional TMGa and ammonia growth. X-ray, Hall, and atomic force microscopy (AFM) measurements have been carried out on these samples providing a direct comparison of materials properties associated with these growth precursors. For the DEGaCl-based growth, the x-ray rocking curve line width, using the (0002) reflection, is as low as 300 arcsec on a 2.5-micron thick film. A RMS surface roughness of ~0.5nm measured over a 10x10 micron area.

INTRODUCTION

GaN and related materials have been extensively investigated due to their potential applications in short wavelength optoelectronics and high temperature, high power, high frequency electronics¹. Metalorganic vapor phase epitaxy (MOVPE) and hydride vapor phase epitaxy (HVPE) have been widely used and have generated materials with electrical and optical properties suitable for some device applications². The growth conditions and hence the resulting materials properties in these two systems are different due to the different gallium precursors, operating conditions and reactor structure. MOVPE commonly uses trimethyl gallium or triethyl gallium, which can have complicated gas phase chemistry including the formation of adducts with NH₃. HVPE utilizes GaCl generated *in situ* through the reaction of liquid Ga with HCl. The gas phase chemistry is potentially simpler than in the MOVPE system. Slow gas phase switching times and the general difficulties in growing Al-based materials hamper the use of the HVPE technique to applications involving heterojunctions. GaN produced by the HVPE technique does result in a greatly reduced intensity of the defect-based luminescence referred to as the yellow band (YL) when compared to the TMG-based materials. This has been attributed to the lack of carbon in the HVPE growth system which is present in the growth sources used for MOVPE. Intentional introduction of carbon into HVPE materials can result in the appearance of YL³. If a controlled amount of GaCl can be introduced into a cold wall MOVPE reactor, a low carbon source could be combined with the advantages of the MOVPE reactor environment.

Diethyl gallium chloride (DEGaCl) is used here as a Ga source in GaN growth. DEGaCl will decompose to GaCl through the β -elimination reaction in the gas phase allowing the *in situ* formation of GaCl at relatively low gas phase temperatures:



This source was successfully used in GaAs growth that resulted in high uniformity, low carbon content GaAs film^{4,5}. GaAs selective area growth, with a complete selectivity of GaAs growth with respect to SiO₂, Si₃N₄, and Al₂O₃ masking materials, has been demonstrated over a wide range of process window^{6,7,8}. The temperature range for GaAs using this source was 400-800°C and the higher temperature range of 1000-1150°C, required for conventional GaN growth, has not been investigated. We report here on the use of diethyl gallium chloride (DEGaCl) for the large area growth of GaN within a MOVPE system. The present work demonstrates the utility of the DEGaCl source in GaN epitaxial growth.

EXPERIMENTAL PROCEDURE:

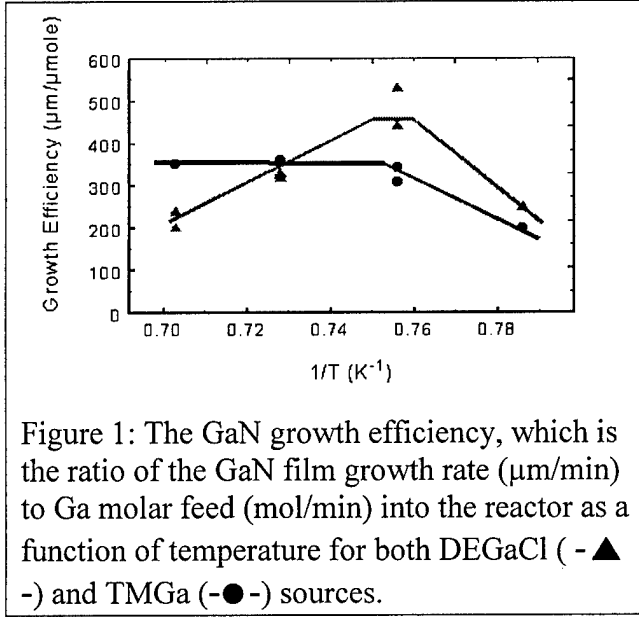
The GaN growth was carried out in a horizontal MOCVD reactor operated at a pressure of 76 Torr. RF induction was used to heat the graphite susceptor. Trimethyl gallium (TMGa), diethyl gallium chloride (DEGaCl) and NH₃ were used as precursors in a hydrogen carrier gas. A disadvantage of the DEGaCl source is its lower vapor pressure requiring both a heated bubbler that was kept at 60 °C and a heated source line to the reactor. Sapphire c-plane substrates were initially etched in H₃PO₄:H₂SO₄=1:3 solution at 70°C for 15 minutes, loaded into the reactor and then heated in a flowing H₂ ambient to 1100°C for 10 minutes prior to the growth. Three comparison sample structures were used in this study. Samples A and C consist of an all DEGaCl or all TMGa-based growth respectively, allowing comparison of the growth chemistry under identical growth process conditions. Sample B is a structure comprised of an initial GaN layer that is identical to Sample C with an additional homoepitaxial GaN layer grown using DEGaCl. Samples A and B have a similar final thickness allowing a comparison of the impact of the initial nucleation of the GaN buffer layer on materials properties. These structures are summarized in Table 1.

All buffer layers were deposited at a temperature of 525°C and heated at a rate of 25°C per minute to 1050°C, then annealed at 1050°C for 10 minutes. The subsequent GaN epilayers in all samples were grown at a temperature of 1000 to 1150°C for 1 hour. The additional GaN layer grown in Sample B using the DEGaCl source was initiated by heating the sample structure (Sample C) to the growth temperature under a high NH₃ partial pressure and directly starting the subsequent growth. The typical gas flows employed were 65 µmol/min for Ga, 4.9 slm for NH₃ and an additional 4 slm for H₂ carrier gas.

Crystalline quality was measured by double crystal x-ray rocking curve at (002) and (104) Bragg peaks. Surface morphology was determined using an atomic force microscope (AFM). Room temperature Hall and C-V measurements were also obtained.

RESULT AND DISCUSSION:

Figure 1 shows the growth efficiency as a function of growth temperature using DEGaCl and TMGa. The growth efficiency (GE) is defined as the thickness of epitaxial film GaN (µm/min) deposited per Ga source flux (µmole/min) in the reactor feed. This calculation considers the TMGa source to be monomeric in the gas phase while DEGaCl gas phase consists of both dimeric and monomeric species. DEGaCl gas phase at 60°C has a dimer mole fraction of 0.75⁹. The GE for both TMGa and DEGaCl increases with increasing temperature over the range 1000 to 1050 °C. At higher temperature, the GE of TMGa source was nearly temperature independent over the range of 1050 °C to 1150 °C, typical of a mass-transport-limited growth. The GE of DEGaCl source, however, decreased with increasing temperature from 1050 °C to 1150 °C. This behavior, we believe, can be attributed to thermodynamic factors. In the case of GaAs growth



growth front has often been considered to be near thermodynamic equilibrium in many cases¹⁰. If this is the case for the high temperature growth of GaN, the supersaturation at the growth front will decrease with increasing temperature due the reversible reaction associated with the HCl reacting at the GaN surface.

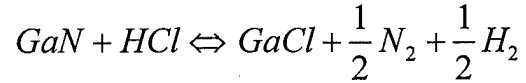
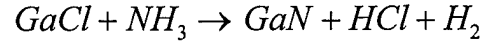
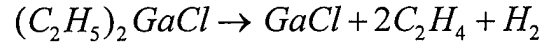
The growth rate of GaN at a temperature of 1050°C as function of the carrier gas flow rate into the bubbler, for both DEGaCl and TMGa, is presented in Figure 2. The Ga flux, n_{Ga} in moles/min, is calculated as:

$$n_{Ga}(Q_{H_2}) = \frac{\alpha Q_{H_2} P_{GaSource}}{22400(P_T - P_{GaSource})},$$

where Q_{H_2} is the flow rate of H_2 carrier gas through the bubbler, $P_{Ga source}$ is the vapor pressure of DEGaCl at the bubbler temperature, P_T is the total pressure within the bubbler, and α is factor describing the degree of associating of the Ga source and assumes a value greater than unity, i.e. $\alpha=1$ for a monomeric source, 2 for a dimeric source, and so on. The DEGaCl source has a much lower vapor pressure (0.5 Torr at 60°C) than TMGa source (30 Torr at -10°C), requiring a larger flow rate of the carrier gas H_2 in order to carry out the same amount of Ga precursor. The GaN growth rate of using TMGa is linearly dependent on Ga flux into the reactor, which is linear with H_2 carrier gas flow rate through the bubbler. The GaN growth rate from DEGaCl may have an indication of saturation at high carrier gas flow rates. This saturation is most probably due to source supply limitations at high carrier gas rates due to the low vapor pressure of the DEGaCl.

Typical AFM images of the GaN surface morphology for sample structures A, B, and C are given in Figure 3. The surface of both Samples A and

from DEGaCl, the growth rate is mass transport limited from 550-850°C, which was the upper limite of the investigated temperature range in that study⁴. The simplest set of chemical reactions important at the GaN growth front in the case of DEGaCl are summarized as:



The last reaction implies equilibrium between the steady state concentrations of HCl and GaCl at the growth front. The MOVPE

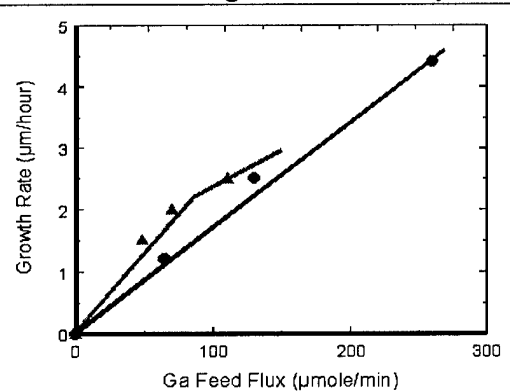


Figure 2. The growth rate of GaN is a function of the calculated Ga flux from the bubbler feed into the reactor for DEGaCl (-▲-) and TMGa (-●-) sources.

B were obtained using DEGaCl source. The GaN surface morphology of these samples is quite smooth with sharp faceted step edges being readily apparent in the micrographs. The Sample C, grown using only the TMGa source for both buffer and high temperature layers, has a morphology typical of MOVPE GaN layers with a smooth surface and meandering steps. The average RMS roughness of Sample A was $\sim 0.5\text{nm}$ measured by AFM over a $10\times 10\text{-micron}$ area. The all-TMGa sample, Sample C, was slightly rougher with a RMS roughness value of $\sim 1.1\text{nm}$. The difference in surface morphology can be attributed to the presence of the GaCl source at the growth front. Vapor phase epitaxy or VPE, utilizing inorganic halogen-based sources, can often lead to more faceted growth than MOVPE. The local thermal-equilibrium at the growth front implies the possibility of an etching or back-reaction reaction as indicated in the chemical reaction scheme outlined above. Surface asperities and defects would be active sites for the removal of GaN from the surface, through these back reactions, resulting in a reduction in surface roughness and the promotion of specific crystal facets. Additionally many chemical impurities form volatile chloride species enabling the possibility of higher purity films at these elevated temperatures.

The measured thin film properties for these structures, grown at 1050°C , are given in Table 1. The x-ray rocking curve line width, using the (0002) reflection, was as low as 300 arcsec on a 2.5-micron thick film for Sample A, utilizing an all- DEGaCl chemistry. The carrier concentration was measured to be as low as $1\times 10^{16}\text{ cm}^{-3}$ by high frequency C-V measurement. Hall data yielded a much higher value for the carrier concentration than C-V data. The carrier concentration in our samples is very high near the initial growth interface due to the highly defected region at the GaN/sapphire interface. The Hall measurement data of Samples B and C can be analyzed by a simple two-layer Hall effect model allows the bulk electrical parameters to be extracted¹¹. We can use the measured properties on Sample C as input into such an analysis, allowing the electrical properties of the subsequently grown DEGaCl-based layer to be

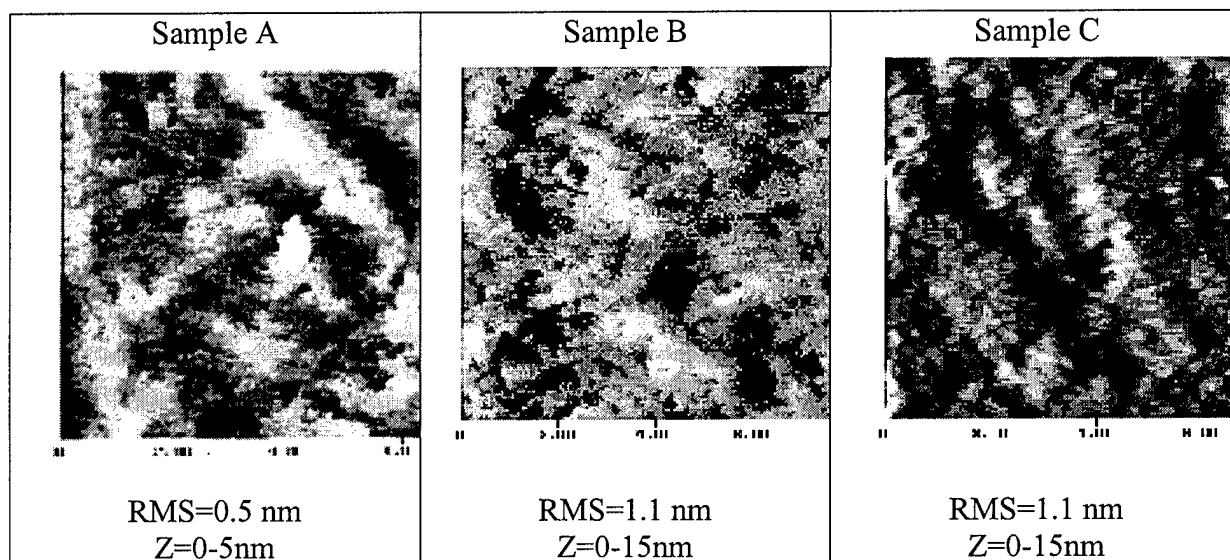


Figure 3: The GaN surface morphology was determined by Atomic Force Microscopy (AFM) for samples grown using DEGaCl or TMGa source. The sample images are obtained over a $10\times 10\text{ micron}$ area. The full range of height (Z) is indicated. The sample structure and related film properties are given in Table 1.

estimated. The calculated results indicate that the top DEGaCl-based GaN film in Sample B had a mobility of $600 \text{ cm}^2/\text{V}\cdot\text{sec}$ and a carrier concentration of $2 \times 10^{16} \text{ cm}^{-3}$, which agrees well with the C-V data on this sample.

Additional DEGaCl-based GaN film properties as a function of temperature and V/III ratio are given in Figure 4. The carrier concentration was measured by C-V technique and the X-ray diffraction rocking curve was measured at both (002) and (104) Bragg reflections. The GaN crystal quality increased with increasing growth temperature over 1000°C to 1100°C . V/III ratio has an optimized value of ~ 3500 at a temperature of 1050°C in our reactor.

Table 1. GaN film properties for sample structures A, B, C grown at 1050°C

Sample Structure	Sample A	Sample B	Sample C
Properties	DEGaCl buffer and high temperature layer	DEGaCl high temperature layer on Sample C	TMGa buffer and high temperature layer
X-ray FWHM (arcsec) at (0002)	300"	550"	700"
RMS Roughness (nm) over $10 \times 10 \mu\text{m}$ area	0.51	1.14	1.18
Hall Concentration (cm^{-3})	1×10^{18}	3×10^{18}	2.5×10^{18}
Hall Mobility ($\text{cm}^2/\text{V}\cdot\text{sec}$)	80	80	62
CV Concentration (cm^{-3})	1×10^{16}	2×10^{16}	2×10^{16}
Thickness (μm)	2.5	$0.7 + 1.5 = 2.2$	1.5

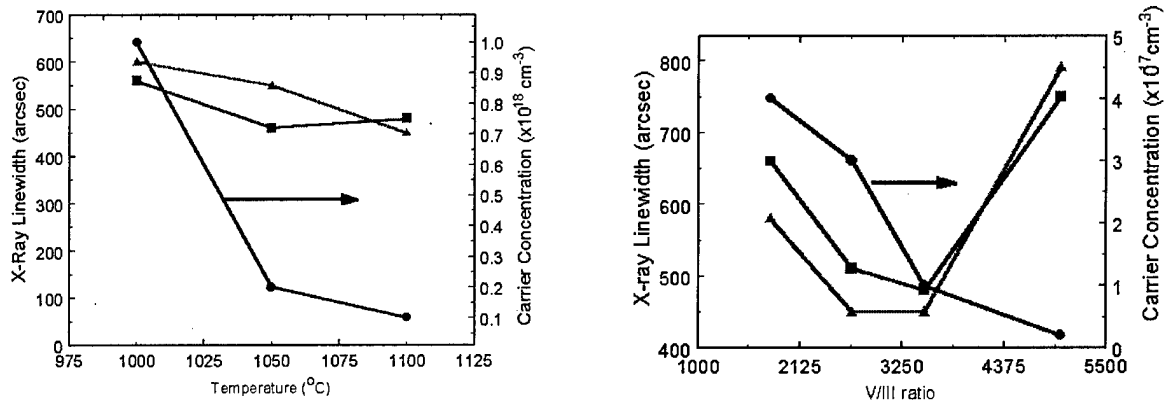


Figure 4: The change in GaN materials properties with growth temperature (Fig. 4a) and inlet V/III ratio (Fig. 4b) were obtained for films grown using the DEGaCl source. The structural quality was measured by x-ray rocking curves about the (002) and (104) Bragg reflections, symbols $\blacktriangle$ and $\blacksquare$ respectively. The carrier concentration ($\bullet$) was obtained by C-V measurement.

SUMMARY:

The diethyl gallium chloride (DEGaCl) source was first studied for GaN growth in a MOVPE reactor. This Cl-based precursor exhibits a difference in growth rate and efficiency from the conventional TMGa-based growth. The DEGaCl-based growth efficiency decreases with increasing temperature indicating that the growth front may be close to local thermodynamic equilibrium. The presence of HCl-related reactions at the growth front can influence the surface morphology and chemical purity by providing reaction pathways for the removal of surface structural and chemical defects and impurities. The DEGaCl source provides a reduced carbon growth chemistry within a MOVPE-based reactor.

ACKNOWLEDGMENTS

The authors would like to thank Aldrich for providing the DEGaCl source. The research funding from the ONR MURI on Compliant Substrates (C. Wood) and facilities support from the NSF UW-Materials Research Science and Engineering Center is gratefully acknowledged.

REFERENCE:

- ¹ H. Morkoc, S. Strite, G. B. Gao, M. F. Lin, B. Sverdlov, and M. Burns, *J. Appl. Phys.* 76, 1363 (1994)
- ² S. Nakamura, G. Fasol, *The blue Laser Diode-GaN light Emitters and lasers (spring-Verlag, Heidelberg, (1997).*
- ³ R. Zhang and T.F. Kuech, *Appl. Phys. Lett.* 72, 1611-1613 (1997).
- ⁴ T. F.Kuech, R.Potemski and F. Cardone *J. Cryst. Growth* V124, 318-325 (1992).
- ⁵ A. Narmann, M.L.Yu *Surface Science* V270, 1041-1047 (1992).
- ⁶ T.F.Kuech *J. Cryst. Growth* V115, 52-60 (1991).
- ⁷ Ko-ichi Yamaguchi, K. Okamoto, *Jpn. J. Appl. Phys.* V32 4885-4888, (1993).
- ⁸ Y. Shiraishi, N. Furuhashi, A. Okamoto, *J. Cryst. Growth* V182, 255-265 (1997) .
- ⁹ N. I. Buchan, R. M. Potemski, and T. F. Kuech, *J. Chem. Eng. Data*, V36, No. 4 (1991).
- ¹⁰ G.B. Stringfellow, *Organometallic Vapor Phase Epitaxy*, (Academic Press, San Diego, 1989) Chap. 3.
- ¹¹ D.C Look, R.J.Molnar, *Appl. Phys. Lett.* 70, 23 (1997).