MOCVD Growth of AlGaN UV LEDs

Jung Han* and Mary H. Crawford

Sandia National Laboratories, MS 0601, Albuquerque, NM 87185-0601

ABSTRACT

Issues related to the MOCVD growth of AlGaN, specifically the gas-phase parasitic reactions among TMG, TMA, and NH_3, are studied using an in-situ optical reflectometer. It is observed that the presence of the well-known gas phase adduct (TMA: NH_3) could seriously hinder the incorporation behavior of TMGa. Relatively low reactor pressures (30-50 Torr) are employed to grow an AlGaN/GaN SCH QW p-n diode structure. The UV emission at 360 nm (FWHM ~ 10 nm) represents the first report of LED operation from an indium-free GaN QW diode.

Keywords: GaN, AlGaN, ultraviolet emitter, gas-phase reaction

1. INTRODUCTION

So far most of the efforts in III-nitride optoelectronic devices have focused on blue light-emitting devices.[1] These devices typically employ AlGaN and/or GaN as wide bandgap confinement layers while adding indium (In) into GaN as active layers to shift the emission into visible spectrum range (λ>400 nm). Shorter wavelength compact UV (λ<370 nm) emitters are of interest for various chemical sensing, flame detection, and possibly optical storage purposes. There are relatively few reports on GaN-based UV emitters. Homojunction GaN p-n diodes have been reported by several groups;[2, 3] the emission is frequently dominated by a blue emission (~430 nm) at low injection level due to carrier recombination involving Mg acceptors. Near band edge emission (~ 380 nm) often emerges as the Mg-related blue emission became saturated by an increased excitation level. Both Amano et al.[4] and Kuga et al.[5] have reported AlGaN/GaN double heterostructure (DH) diodes with emission peaks centered around 375 and 420 nm, respectively. In both cases the widths of emission peaks are in excess of 250 meV (or 40 nm), indicative of recombination through localized centers.

It is known that low-dimensional heterostructures (such as quantum wells, QWs) can provide carrier confinement and enhance optical efficiency. Much studies in nitride-based emitters have been devoted to the growth and characterization of InGaN QWs.[6] The mechanism of efficient light emission and identification of microstructural signatures remain subjects of intense debate. Indium-free GaN QWs received relatively little attention. Photoluminescence (PL) has been applied to undoped[7] and Si-doped[8] AlGaN/GaN quantum wells (QWs) with linewidths varying from 80 to 110 meV at room temperature. Stimulated emission by optical pumping was also achieved in the latter report. There has been no report, to the best of our knowledge, on the incorporation of AlGaN/GaN QWs into a p-n diode configuration. In this paper we will report the metal-organic chemical vapor depostion (MOCVD) of AlGaN, as well as electrical and optical characterization of AlGaN/GaN separate-confinement heterostructure (SCH) QW p-n diodes. The effect of TMA:NH_3 reaction on the growth rate was studied *in situ* using an optical reflectance monitor[9] which enables us to delineate the susceptibility to pre-reactions over a wide gas compositions. We will show that the formation of (TMA:NH_3) adduct not only depletes TMA from vapor state but also indirectly inhibits the incorporation of TMG (by as much as 60%). The understanding of gas-phase chemistry enabled us to grow an AlGaN/GaN SCH QW diode structure which was subsequently processed into a LED. The observed emission at 360 nm from a AlGaN/GaN SCH QW diode is the shortest wavelength reported from a GaN-based injection device. An linewidth of about 90 meV (at room temperature) suggests that the emission is from band-to-band recombination.

2. EXPERIMENTAL SETUP

GaN/AlGaN was grown in a high speed rotating (~ 1200 rpm) MOCVD reactor (diameter of the quartz chamber is 4.75"). Two-inch basal plane sapphire wafers were placed on a molybdenum (Mo) susceptor which is RF inductively heated using a SiC-coated graphite coupling block. Temperature was monitored by a pyrometer focusing on the Mo susceptor surface nearly co-planar with the wafer surface. Ammonia (NH_3), Trimethylgallium (TMGa), and Trimethylaluminum (TMAl) were

* jhan@sandia.gov, Tel: (505)284-4531, Fax: (505)844-3211

DISCLAIMER

used as the N, Ga, and Al precursors, respectively. Hydrogen (H_2) was used as the carrier gas and also to supplement the NH_3 in making up the required flow rate as determined by the reactor pressure and wafer rotating speed.[10] Metal-organic precursors were separated from hydride gases before being injected into top of the growth chamber. An in-situ reflectometer uses a tungsten lamp as a light source, illuminating a spot (of 6 mm in diameter) on the sample surface through the reactor port window. Standard two-step growth (550 and 1050 °C for the low and high temperatures, respectively) with GaN low-temperature buffer layer (~250 Å) was used in this work.[11] A GaN:Si (n ~ $2x10^{18}cm^{-3}$) layer of 3 μm thick was first grown on the LT buffer.

3. ALGAN GAS PHASE REACTION

Figure 1 shows a typical reflectance trace during the particular experiment. In this experiment the TMGa and TMAl flow rates were fixed at around 60 μmole/min. The reflectance trace provides a convenient means to determine the growth rate *in situ* from the periodicity of Fabry-Perot interference oscillations. TMGa, TMAl, and both TMGa and TMAl were open sequentially to allow a measurement of the growth rates of GaN (region (i)), AlN (region (ii)), and AlGaN (region (iii)), respectively, at a given gas composition. We then change the gas composition (partial pressures of H_2 and NH_3 independently, from region (I) to (II) in Fig. 1) and repeat the same valve operation.

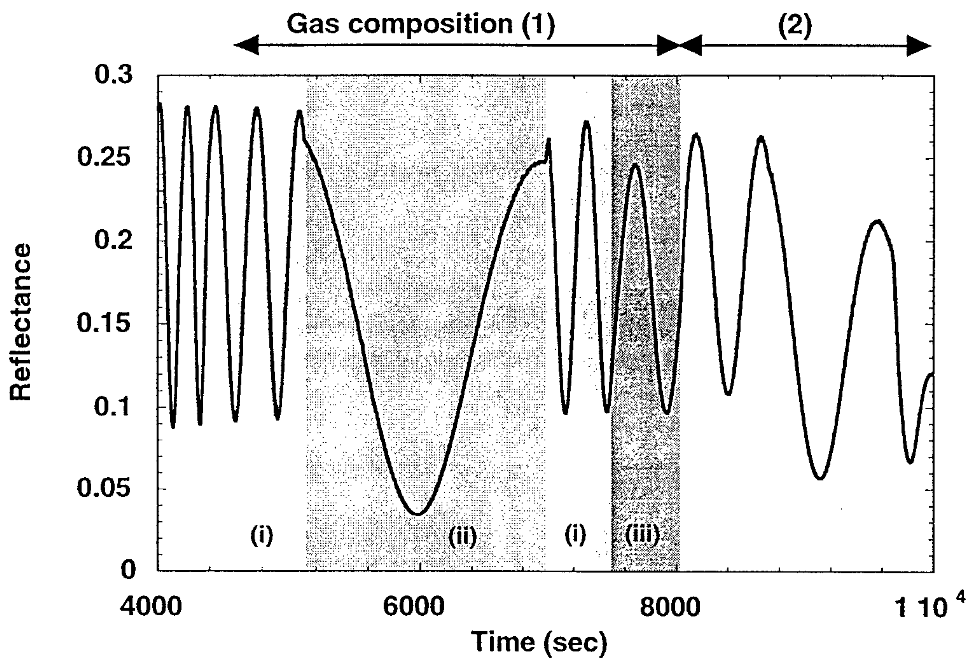

Figure 1. In-situ reflectance trace during a study of the gas-phase reactions among TMA, TMGa, and NH_3.

Such an *in-situ* probe enables the construction of three-dimensional plots of the growth rates of GaN (Fig. 2(a)), AlN (Fig. 2(b)), and AlGaN (Fig. 2(c)) versus partial pressures of both H_2 and NH_3. In Figure 2(a) the growth rate of GaN increases slightly with the increase of NH_3 pressure (when the H_2 pressure is less than 20 Torr). It is clear from Fig. 2(a) that the reported gas phase reactions[12] between TMGa and NH_3 does not result in much (if any) decrease of growth efficiency. The decrease of growth rate along H_2 axis is likely due to the effect of hydrogen-assisted etching or desorption of GaN. The trend of the growth rate of AlN versus NH_3 shows distinctly different behavior. An increase of NH_3 leads to a rapid decrease of AlN incorporation (when the H_2 pressure is below 20 Torr). We note that the above observation is in qualitative agreement with the previous report.[13] The growth rate of AlGaN (with both TMGa and TMAl open) is shown in Fig. 2(c). It is interesting to note that the measured growth rate of AlGaN is always less than the sum of the growth rates of the individual binary compounds. An "interaction parameter" Ω is defined as (GR_{AlGaN}/(GR_{AlN} + GR_{GaN})) which is plotted in Fig. 2(d). An Ω with value approaches unity suggests an independent and additive incorporation for the TMAl and TMGa. On the other hand an Ω much less than unity implies that an additional interaction, either in the gas phase or on the gas-solid interface, between the respective adducts has inhibited the incorporation of certain species. Comparing Fig. 2(b) and 2(d), one could argue that the reduction of Ω follows the general trend of the reduction of AlN growth rates (which in turn suggest an increase of adducts, most likely $[(CH_3)_2Al:NH_2]_n$,[14] in the gas phase). The presence of $TMAl:NH_3$ adducts is seen to inhibit the incorporation of TMGa, down to less than 40% at an NH_3 partial pressure of 58 Torr. We speculated that the reduction of TMGa incorporation is possibly due to either a scavenging effect of the of $TMAl:NH_3$ adducts on TMGa in the gas phase, or alternatively a site-blocking effect due to the $TMAl:NH_3$ adducts on the gas-solid interface. The presence of such interaction between TMGa and $[TMAl:NH_3]$ adduct could seriously affect the controllability of Al alloy fraction and growth uniformity. A reactor pressure of 30 to 50 Torr was subsequently used to alleviate gas-phase reactions.

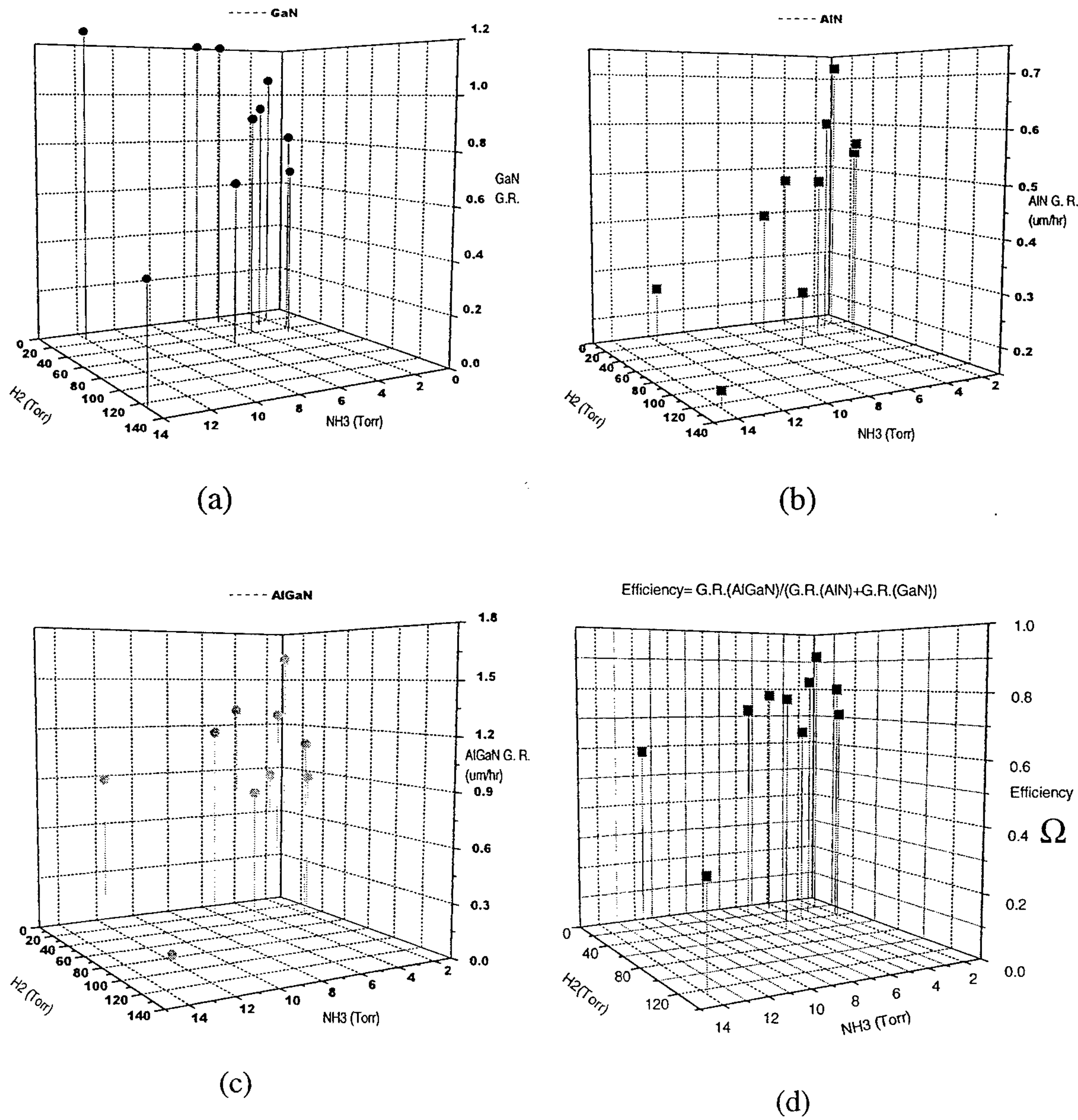

Figure 2. Growth rate versus gas compositions for GaN (a), AlN (b), and AlGaN (c). The interaction parameter Ω (see text for explanation) as a function of gas pressures is plotted in (d).

4. ALGAN/GAN QW LEDs

The LED structure consists of an $Al_{0.2}Ga_{0.8}N$:Si (n ~ $2x10^{18}cm^{-3}$) cladding layer of 0.4 μm thick, an $Al_{0.1}Ga_{0.9}N$:Si (n ~ $2x10^{17}cm^{-3}$) wave-guiding layer of 0.09 μm thick, four GaN quantum wells (~ 30Å undoped) separated by undoped $Al_{0.1}Ga_{0.9}N$ barrier layers, a p-$Al_{0.1}Ga_{0.9}N$ ([Mg] ~ $2x10^{19}cm^{-3}$) wave-guiding layer of 0.09 μm thick, a p-$Al_{0.2}Ga_{0.8}N$ ([Mg] ~ $1x10^{20}cm^{-3}$) cladding layer of 0.4 μm thick, and a p-GaN ([Mg] ~ $1x10^{20}cm^{-3}$) contact layer of 0.3 μm thick. We note that the in-situ reflectometer enabled us to monitor the extend of gas-phase pre-reactions among TMAl, TMGa, and NH_3. Significant gas-phase reactions occurred between TMAl and NH_3 when reactor pressure exceeded 80 Torr. The TMAl: NH_3 adduct not only depletes TMAl from the gas stream but also inhibits the incorporation of TMGa which will be the subject of a separate publication.[15] For the SCH structure reported here, the LT GaN and the Si-doped GaN were grown at 140 Torr, the rest of the structure was grown between 30 to 40 Torr. After growth the AlGaN/GaN SCH sample was annealed in the reactor at 850°C under flowing nitrogen (140 Torr) for 20 min to activate the Mg acceptors. The sample was etched (using inductively-coupled plasma etching) 1.5 μm deep to expose the n-GaN region. Ni/Au and Ti/Au were employed as p- and n-type contacts, respectively.

Figure 3(a) shows the current-voltage (I-V) characteristics of a processed diode with a mesa diameter of 100 μm. The top p-type contact has a circular ring pattern to facilitate light emission from the center of the mesa. We note, however, that the limited p-type conductivity in GaN and AlGaN significantly limits lateral current spreading and the effective device area is much less than the physical dimension of the mesa. The forward turn-on occurs at around 4 V even though the impedance is high compared to a separate homojunction GaN p-n diode (10mA at 10 V) of comparable size. Electroluminescence (EL) is collected using a fiber positioned at about 3 mm from the edge of the device. Figure 3(b) shows the EL spectrum at different injection current from a device of 250 μm in diameter. The emission at 360 nm agrees well with the PL peak position reported earlier,[7,8] and is the shortest wavelength reported from a GaN-based light emitting diode. The FWHM of the emission peak is around 10 nm which compares favorably with the reports of 30 to 45 nm from GaN-based DH diodes. We are in the process of measuring the integrated light output power as well as the quantum efficiency, the results will be reported elsewhere.

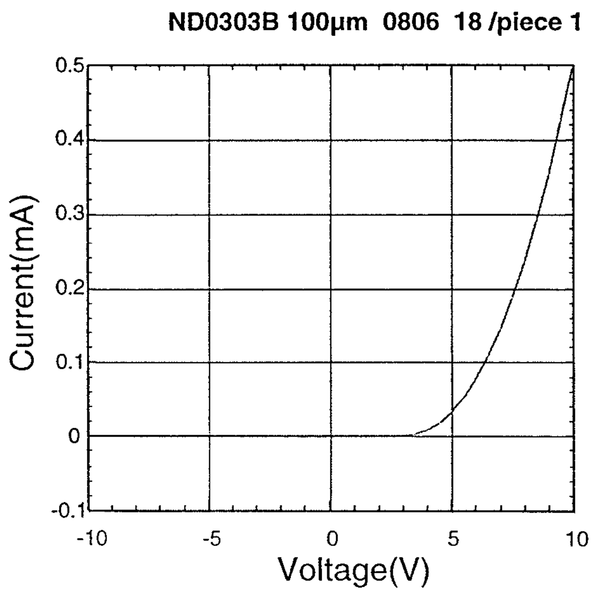

Figure 3(a)

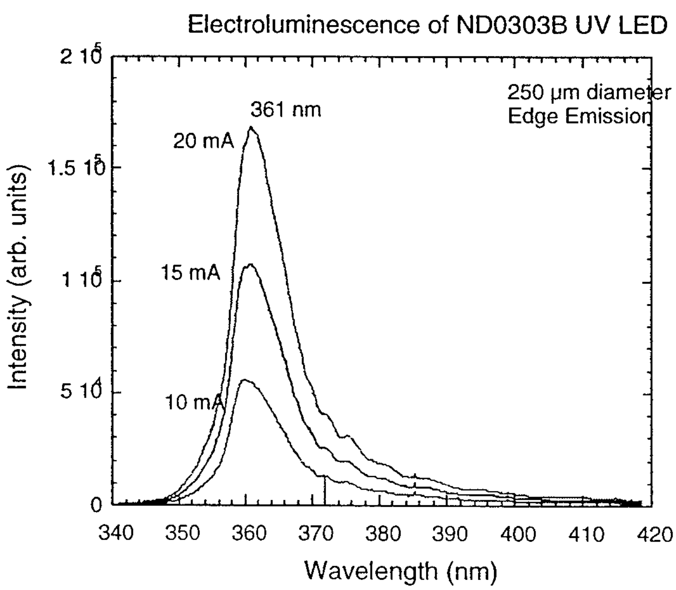

Figure 3(b)

Figure 3. Diode I-V (a) and luminescence spectrum (b) from an AlGaN/GaN p-n SCH QW LED.

5. CONCLUSION

In conclusion, we have studied the gas-phase reactions during the MOCVD growth of AlGaN. The presence of [TMA:NH_3] adduct appeared to hinder the incorporation of TMGa, possibly through a gas-phase scavenging or surface site blocking effect. An AlGaN/GaN p-n QW LED was grown at reduced reactor pressure regime. The observed UV emission at 360 nm represents the shortest wavelength emission from a GaN-based injection device.

6. ACKNOWLEDGEMENT

Technical inputs from The authors acknowledge technical support from J. J. Figiel and M. Banas. Discussions with H. Amano (Meijo University), R. M. Biefeld, W. G. Breiland, and A. F. Wright are also acknowledged. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

7. REFERENCES

[1] Nakamura and G. Fasol, *The Blue Laser Diode*, Springer-Verlag, Berlin Heidelberg (1997).

[2] I. Akasaki, H. Amano, H. Murakami, M. Sasa, H. Kato, and K. Manabe, "Growth of GaN and AlGaN for UV/blue p-n junction diodes", *J. Cryst. Growth 128*, 379 (1993).

[3] M. Asif Khan, Q. Chen, R. A. Skogman, and J. N. Kuznia, "Violet-blue GaN homojunction light emitting diodes with rapid thermal annealed p-type layers", *Appl. Phys. Lett. 66*, 2046 (1995).

[4] I. Akasaki and H. Amano, "Room temperature ultraviolet/blue light emitting devices based on AlGaN/GaN multi-layered structure", p327, *Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials*, Tsukuba (1992).

[5] Y. Kuga, T. Shirai, M. Haruyama, H. Kawanishi, and Y. Suematsu, "Violet and near-UV light emission from GaN/$Al_{0.08}Ga_{0.92}N$ injection diode grown on (0001) 6H-SiC substrates by low-pressure metal-organic vapor phase epitaxy", *Jpn. J. Appl. Phys. 34*, 4085 (1995).

[6] For example, C. J. Sun, M. Zubair, Q. Chen, J. W. Yang, M. Asif Khan, M. S. Shur, A. D. Bykhovski, Z. Liliental-Weber, C. Kisielowski, M. Smith, J. Y. Lin, and H. X. Xiang, "Quantum shift of band-edge stimulated emission in InGaN-GaN multiple quantum well light emitting diodes", *Appl. Phys. Lett. 70*, 2978 (1997); C. K. Sun, S. Kellar, G. Wang, M. S. Minsky, J. E. Bowers, and S. P. DenBaars, "Radiative recombination lifetime measurements of InGaN single quantum well", *Appl. Phys. Lett. 69*, 1936 (1996); and E. S. Jeon, V. Kozlov, Y. K. Song, A. Vertikov, M. Kuball, A. V. Nurmikko, H. Liu, C. Chen, R. S. Kern, C. P. Kuo, and M. G. Craford, "recombination dynamics in InGaN quantum wells", *Appl. Phys. Lett. 69*, 4194 (1996).

[7] M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, W. Kim, and H. Morkoc, "Optical transition in GaN/AlGaN multiple quantum wells grown by molecular beam epitaxy", *Appl. Phys. Lett. 69*, 2453 (1996).

[8] T. J. Schmidt, X. H. Yang, W. Shan, J. J. Song, A. Salvador, W. Kim, O. Aktas, A. Botchkarev, and H. Morkoc, "Room-temperature stimulated emission in GaN/AlGaN separate confinement heterostructure grown by molecular beam epitaxy", *Appl. Phys. Lett. 68*, 1820 (1996).

[9] J. Han, T. -B. Ng, R. M. Biefeld, M. H. Crawford, and D. M. Follstaedt, "The effect of hydrogen on morphology evolution during GaN metalorganic chemical vapor deposition", *Appl. Phys. Lett. 71*, 3114 (1997).

[10] W. G. Breiland and G. H. Evans, J. Electrochem. Soc. 138, 1806 (1991).

[11] T. -B. Ng, J. Han, R. M. Biefeld, and M. V. Weckwerth, "In-situ reflectance monitoring during MOCVD of AlGaN", *J. Electron. Mat.* April (1998).

[12] A. Thon and T. F. Kuech, "High temperature adduct formation of Trimethylgallium and ammonia", *Appl. Phys. Lett. 69*, 55 (1996).

[13] C. H. Chen, H. Liu, D. Steigerwald, W. Imler, C. P. Kuo, M. G. Craford, M. Ludowise, S. Lester, and J. Amano, "A study of parasitic reactions between NH_3 and TMGa or TMAl", *J. Electro. Mat. 25*, 1004 (1996).

[14] L. V. Interrante, G. A. Sigel, M. Garbauskas, C. Hejna, and G. A. Slack, "Organometallic precursors to AlN: synthesis and crystal structures of $[(CH_3)_2AlNH_2]_3$ and the planar species $[(t\text{-}C_4H_9)_2AlNH_2]_3$", *Inorg. Chem. 28*, 257 (1989).

[15] J. Han, J. J. Figiel, R. M. Biefeld, and M. E. Martram (unpublished).

M98005911

Report Number (14) SAND--98-1399C
CONF-980729--

Publ. Date (11) 1998
Sponsor Code (18) DOE/DP , XF
UC Category (19) UC-700 , DOE/ER

ph

19980720 068

DOE