

Chemical vapor deposition of aluminum and gallium nitride thin films from metalorganic precursors

David M. Hoffman^{a)} and Sri Prakash Rangarajan
Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Satish D. Athavale and Demetre J. Economou^{a)}
Department of Chemical Engineering, University of Houston, Houston, Texas 77204-4792

Jia-Rui Liu, Zongshuang Zheng, and Wei-Kan Chu
Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5932

(Received 17 July 1995; accepted 11 November 1995)

Nearly stoichiometric aluminum and gallium nitride thin films were prepared from hexakis(dimethylamido)dimetal complexes, $M_2[N(CH_3)_2]_6$ ($M=Al,Ga$), and ammonia at substrate temperatures as low as 200 °C by using low pressure thermal and plasma enhanced chemical vapor deposition (CVD). Both processes gave films that showed little or no carbon (<5 at. %) and no oxygen (<few at. %) contamination, but in all cases there was hydrogen incorporation. The films were highly transparent in the ultraviolet and visible regions. The barrier properties of the aluminum nitride films in a Si/AlN/Au metallization scheme were examined by using backscattering spectrometry. The growth rate of the aluminum nitride films was as high as 1300 Å/min. Overall, the results suggest that $M_2[N(CH_3)_2]_6$ ($M=Al,Ga$) are promising precursors for low-temperature/low-pressure thermal and plasma-enhanced CVD of group III nitride thin films. © 1996 American Vacuum Society.

I. INTRODUCTION

Aluminum nitride has a large direct band gap of 6.2 eV, high thermal conductivity (up to 320 W/m K), high decomposition temperature (≈ 2700 K), and it is chemically inert and transparent in the visible and near infrared regions. Because of these properties, AlN thin films have great potential for microelectronic and optoelectronic devices.¹ Gallium nitride has a direct band gap of 3.4 eV, a predicted large saturated electron drift velocity, and is transparent in the visible and near infrared regions. GaN is a promising material for light emitting diodes and ultraviolet (UV) lasers, and it is a candidate for use in high frequency, high power devices.² Both AlN and GaN have piezoelectric properties and high acoustic velocities that make them attractive for use in acoustic devices, and alloys of the group III nitrides, such as AlGaIn and GaInN, have potential applications in microelectronics and optoelectronics.³

Recently, the low temperature (<400 °C) atmospheric pressure chemical vapor deposition (APCVD) of nearly stoichiometric aluminum and gallium nitride thin films from $M_2[N(CH_3)_2]_6$ ($M=Al,Ga$) and ammonia precursors was reported.^{4,5} We were interested in determining whether the $M_2[N(CH_3)_2]_6/NH_3$ precursor system could be used to produce stoichiometric films at low temperatures in low pressure thermal and plasma enhanced CVD processes. The low temperature deposition of stoichiometric films is especially important for gallium nitride where nitrogen site vacancies are thought to cause the high n -type backgrounds commonly observed for this material.^{2,6} Herein we report that nearly stoichiometric aluminum and gallium nitride are deposited at

temperatures as low as 200 °C by using $M_2[N(CH_3)_2]_6$ ($M=Al,Ga$) (Fig. 1) and ammonia in a low pressure thermal CVD process and $M_2[N(CH_3)_2]_6$ ($M=Al,Ga$) and plasma-activated ammonia in a plasma process. This article is a companion to our previous articles where we reported on the low temperature deposition of high quality silicon, germanium, and tin nitride thin films by using the corresponding tetraakis(dimethylamido)metal complexes and plasma activated ammonia.^{7,8}

II. EXPERIMENT

The precursors used in this study, $Al_2[N(CH_3)_2]_6$ and $Ga_2[N(CH_3)_2]_6$, were prepared by the literature methods.⁹ Their purity (>98%) was checked by ¹H nuclear magnetic resonance (NMR). Both complexes are moderately air-sensitive solids that readily sublime under vacuum (10^{-2} Torr) in the temperature range 70–80 °C.⁹

The experimental CVD apparatus (Fig. 2) has been described previously.^{7,8} It is a low pressure, cold wall quartz tubular reactor with an inside diameter of 3.5 cm. Undiluted ammonia (Matheson, ULSI purity) was fed through one end of the tube, while the metalorganic precursor was injected downstream just before the substrate. The temperature of the heated substrate platform was monitored by a thermocouple. System base pressures of <3 mTorr were achieved before each deposition. When a plasma enhanced deposition was carried out, an induction coil connected to a 13.56 MHz power supply through an impedance matching network was used to generate the plasma. The net power input was 20–25 W. Only the ammonia was passed through the plasma. The substrate itself was not directly in the plasma, but a diffuse glow encompassed it. The same configuration was used for

^{a)}Authors to whom correspondence should be addressed.

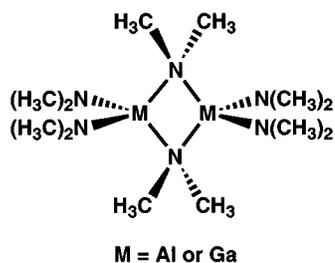


FIG. 1. Structure of the hexakis(dimethylamido)dimetal complex. The metal can be M=Al or Ga.

the thermal depositions, except the plasma generator was turned off. Ultrahigh purity helium was passed through the reactor as the substrate was heated to the desired deposition temperature and during cool down after deposition. Substrate handling and film characterization techniques were carried out as described previously.^{7,8}

III. RESULTS

A. General growth conditions and film properties

The $M_2[N(CH_3)_2]_6$ complexes and ammonia gave film growth on silicon and quartz substrates both with and without plasma activation of the ammonia at 200–400 °C. The precursor flasks were heated to 90–100 °C to facilitate transfer of the precursor vapors to the reaction zone. The flow rate of undiluted ammonia was 150 sccm, and the precursor flow rate was approximately 5% of the ammonia flow rate.

The deposited films varied in thickness along the substrate diagonal with the thickest part near the precursor inlet tube. All the films were smooth and adhered well to the substrates as judged by the Scotch tape test.¹⁰ They gave the rainbow-like interference patterns typically observed for films with high refractive indexes.

X-ray diffraction was used to examine the crystallinity of selected aluminum nitride (plasma deposited at 388 °C on silicon and thermally deposited at 292 °C on silicon) and gallium nitride (plasma deposited at 312 °C on silicon and thermally deposited at 303 °C on silicon) films. The absence of any peaks in the diffraction spectra of these films suggests that they are amorphous.

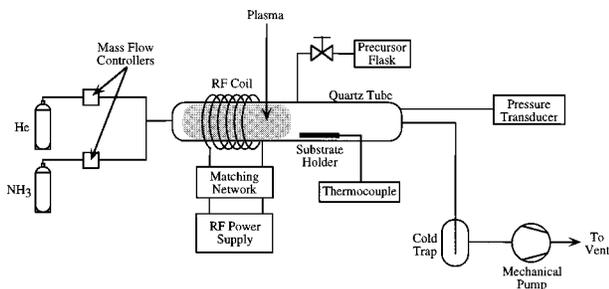


FIG. 2. Schematic of the experimental apparatus. For thermal CVD experiments to plasma were not used.

TABLE I. Compositions and refractive indexes of aluminum nitride films deposited from $Al_2(NMe_2)_6$ and NH_3 or $Al_2(NMe_2)_6$ and plasma-activated NH_3 .

Temperature (°C)	N/Al ratio ^c	C/Al ratio (at. %)	H/Al ratio (at. %) ^d	Refractive index
202 ^a	1.0	n.o. ^e	0.24 (12)	2.03
296 ^a	1.1	0.05 (2.4)	0.30 (14)	1.85
388 ^a	1.0	0.04 (3.43)	0.28 (14)	1.95
202 ^b	1.0	0.03 (2.95)	0.22 (11)	1.90
292 ^b	1.2	0.06 (2.65)	0.33 (15)	2.34
392 ^b	1.2	0.08 (4.18)	0.25 (11)	2.03

^aThe plasma was on: plasma power was 20–25 W. The NH_3 flow rate was 150 sccm. The metalorganic precursor flow rate was ≈ 7.5 sccm.

^bThe plasma was off. The NH_3 flow rate was 150 sccm.

^cThe error is estimated to be ± 0.1 .

^dA density of 3.26 g/cm³ was assumed for aluminum nitride. The error in the H/Al ratio is estimated to be ± 0.06 .

^eA carbon signal was not observed in the backscattering spectrum.

Previous experiments have shown that thermally decomposing the amido compounds (i.e., no plasma or ammonia) produces films with large amounts of carbon contamination.^{4,5} We carried out two control depositions to determine if the precursors would perhaps give clean nitride films with the plasma power on, but with no ammonia flowing. Under these conditions, both metalorganic complexes gave carbon-contaminated films (≈ 10 –20 at. % as determined by backscattering spectrometry) at ≈ 300 °C. This indicates that the plasma-activated ammonia serves to rid the metalorganic precursors of carbon, as in the previous APCVD^{4,5} and low pressure plasma activated depositions.^{7,8}

B. Aluminum nitride films

Compositional data and refractive indexes as a function of deposition temperature for aluminum nitride films deposited on silicon from $Al_2[N(CH_3)_2]_6$ and NH_3 with and without plasma activation are presented in Table I.

The growth rates for the plasma deposited films (550–1300 Å/min) were significantly higher than for the thermally deposited films (< 125 Å/min). In both cases there was an increase in growth rates as a function of deposition temperature. For comparison, AlN films deposited by APCVD from $Al_2[N(CH_3)_2]_6$ and NH_3 had growth rates of ≈ 1000 Å/min at 100–400 °C.⁴ Films deposited from $[(CH_3)_2AlNH_2]_3$ in a low pressure CVD system had growth rates of 5–25 Å/min at substrate temperatures of 400–800 °C,¹¹ and films deposited from $[(CH_3CH_2)_2AlN_3]_3$ at low pressure had growth rates of ≈ 13 Å/min at 500 °C.¹² Plasma CVD films deposited using trimethylaluminum and NH_3 at 300 °C with a plasma power of 20–250 W had growth rates of < 200 Å/

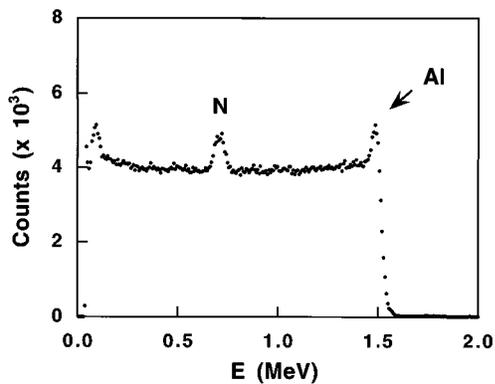


FIG. 3. Backscattering spectrum for an aluminum nitride film deposited on silicon at 296 °C from $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$ and plasma activated ammonia. Beam: 3.3 MeV He^{2+} .

min, and at 250 °C with a plasma power of 500 W the growth rates were $\approx 40 \text{ \AA}/\text{min}$.^{13,14}

Infrared (IR) spectra for all aluminum nitride films show an intense absorption band at around 660 cm^{-1} assigned to the Al–N stretch.^{11,13,14} A broad very weak band observed at $\approx 3300 \text{ cm}^{-1}$ in some of the spectra is probably due to N–H stretches,^{11,13,16} although bands in this region have also been interpreted as resulting from carbon impurities.¹⁶ A weak band is also observed in most of the spectra at $\approx 2120 \text{ cm}^{-1}$. Hasegawa *et al.* assigned a band they observed at 2200 cm^{-1} for plasma AlN films to Al–H stretches.¹⁴ It is unlikely, however, that Al–H bonds would be formed from the amido precursors and ammonia in the low temperature thermal depositions if one assumes the deposition mechanism involves transamination and α -hydrogen elimination as proposed in previous APCVD studies.^{4,5} Others have interpreted bands at around 2200 cm^{-1} as possibly arising from $\text{C}\equiv\text{N}$ impurities.^{16–18} Appropriate labeling studies need to be carried out to unequivocally assign the 3300 and 2120 cm^{-1} bands.

N/Al ratios for the plasma and thermally deposited films are close to the ideal stoichiometry of 1:1 as determined by backscattering spectrometry (Fig. 3).^{19,20} In our best films we do not observe oxygen peaks in the backscattering spectrum, but carbon is usually observed ($<5 \text{ at. \%}$). The carbon content was not reduced by increasing the proportion of ammonia in the flow. The atmospheric pressure CVD aluminum nitride films deposited from $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 were also nearly stoichiometric.⁴ Films deposited from trimethylaluminum and a NH_3 plasma (300 °C, 20–250 W) using H_2 or N_2 as the carrier gas had an excess of aluminum (≈ 10 – 18 at. \%).¹⁴ AlN films deposited from $[(\text{CH}_3)_2\text{AlNH}_2]_3$ at low pressure were nearly stoichiometric¹¹ while films deposited from $[\text{R}_2\text{Al}(\mu\text{-N}_3)]_3$ ($\text{R}=\text{CH}_3, \text{CH}_2\text{CH}_3$) had varying amounts of aluminum, nitrogen, and carbon depending on the deposition conditions.¹²

According to elastic recoil detection (ERD) measurements,^{19,21} our plasma and thermally deposited films have hydrogen contents that vary between 11–15 at. %. AlN films prepared from $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 by the APCVD

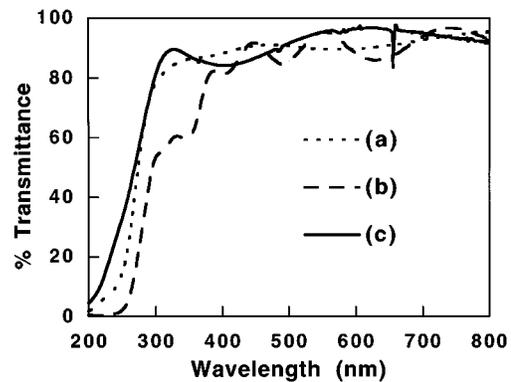


FIG. 4. Transmission spectra of aluminum nitride films deposited from $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$ and plasma-activated NH_3 at (a) 197, (b) 293, and (c) 388 °C on quartz.

technique had 18–37 at. % of hydrogen, the amount depending on the deposition temperature.⁴

The transmittance spectra of plasma deposited aluminum nitride films on quartz are shown in Fig. 4. Films prepared by both plasma and thermal CVD had transmittances of 85%–90% in the visible and near-IR regions. The peak transmittance did not vary appreciably with deposition temperature. The optical gaps for the plasma deposited films, determined by plotting d^2E^2 vs E (where d =optical density and E =photon energy)²² varied between 4.5 and 5.2 eV with no apparent systematic variation of the band gaps with deposition temperature (202–392 °C). Films deposited at 197 and 293 °C using the plasma technique exhibited two tangents in the d^2E^2 vs E plots, one corresponding to a lower and the other to a higher value of the band gap. It is likely that the lower value arises from a carbon impurity band beneath the conduction band.¹⁶ The band gaps for the thermally deposited AlN films are similar (4.5–5.5 eV) to those for the plasma deposited films.

As a comparison, band gaps for AlN films deposited from $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 in the APCVD process were 5.0–5.8 eV, depending on the deposition temperature.⁴ Band gaps for plasma-deposited AlN films using trimethylaluminum and NH_3 as precursors at 300 °C were reported to be 5.3–5.6 eV,¹⁴ and films produced from the plasma chemical reaction of AlCl_3 and N_2 at 700–1300 °C had band gaps of 5.9–6.0 eV.²³ The band gap of epitaxially grown AlN is 6.2 eV.²⁴

The refractive indexes of the plasma and nonplasma deposited AlN films are also listed in Table I. The refractive indexes varied between 1.85 and 2.03 for the plasma-deposited films and between 1.90 and 2.34 for the thermally deposited films. The variation in the refractive indexes is probably due to the varying stoichiometries and impurity concentration, which affect the film densities and thereby the refractive indexes of the films. The reported refractive indexes of polycrystalline aluminum nitride films deposited by APCVD from $\text{Al}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 were 1.65–2.04.⁴ The refractive index of single crystalline AlN is 2.16.²⁵

The diffusion barrier properties of the aluminum nitride

TABLE II. Compositions and refractive indexes of gallium nitride films deposited from $\text{Ga}_2(\text{NMe}_2)_6$ and NH_3 or $\text{Ga}_2(\text{NMe}_2)_6$ and plasma-activated NH_3 .

Temperature (°C)	N/Ga ratio ^c	C/Ga ratio (C at. %)	H/Ga ratio (H at. %) ^d	Refractive index
190 ^a	1.3	0.09 (3.82)	0.62 (27)	2.06
294 ^a	1.1	0.06 (3.39)	0.27 (13)	2.19
377 ^a	1.1	0.08 (3.86)	0.27 (13)	2.37
183 ^b	1.3	0.13 (5.22)	0.67 (27)	1.99
301 ^b	1.2	n.o. ^e	0.52 (23)	2.04
389 ^b	1.2	0.09 (4.18)	0.32 (14)	1.83

^aThe plasma was on; plasma power was 20–25 W. The NH_3 flow rate was 150 sccm. The metalorganic precursor flow rate was ≈ 7.5 sccm.

^bThe plasma was off. The NH_3 flow rate was 150 sccm.

^cThe error in the determination of the N/Ga ratio is ± 0.1 .

^dA density of 6.1 g/cm^3 was assumed for gallium nitride. The error in the H/Ga ratio is estimated to be ± 0.06 .

^eA carbon signal was not observed in the backscattering spectrum.

films were investigated for a Si/AlN/Au metallization scheme.²⁶ A 800-Å-thick aluminum nitride layer on silicon with a 500-Å-thick gold overlayer was subjected to thermal treatment at 518 °C for ≈ 1 h under a 100 sccm flow of helium. During the annealing the shiny gold surface became noticeably duller. Backscattering spectra were taken before and after annealing. The spectra show that there is slight interdiffusion of the gold overlayer into the aluminum nitride, but none into the silicon substrate. Scanning electron microscopy (SEM) micrographs of the annealed sample show the surface of the annealed film has a rough texture, probably due to the formation of etch pits at high temperatures,²⁶ and some nodular structures.

C. Gallium nitride films

Film compositional data and refractive indexes as a function of temperature for gallium nitride films deposited from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 with and without plasma activation are given in Table II.

The growth rates varied between 133 and 192 Å/min for the plasma-deposited films and between 175 and 275 Å/min for the thermally deposited films at substrate temperatures of 183–389 °C. These rates are lower than those observed for films deposited by the APCVD technique from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 , where growth rates of 1000–1500 Å/min at 100–400 °C were observed.⁵ The reported growth rates for plasma-deposited gallium nitride films from trimethylgallium and ammonia at temperatures of 315–520 °C and rf powers of 20–80 W were 0.8–50 Å/min.²⁷ GaN films prepared from gallium and nitrogen by electron cyclotron resonance (ECR) plasma deposition with a source power of ≈ 250 W had a growth rate of ≈ 33 Å/min.²⁸ GaN films deposited from GaCl_3 and ammonia in an APCVD reactor at ≈ 550 °C had growth rates of 50–250 Å/min,²⁹ and the ther-

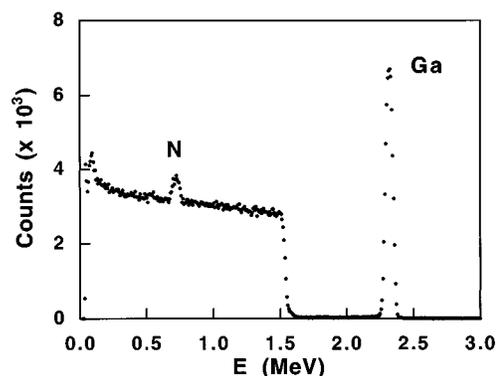


Fig. 5. Backscattering spectrum for a gallium nitride film deposited on silicon at 291 °C. Beam: 3.3 MeV He^{2+} .

mal decomposition of diethylgallium azide in a APCVD reactor produced GaN films at a rate of ≈ 40 Å/min.³⁰

IR spectra for the gallium nitride films show a prominent peak at 550 cm^{-1} assigned to the Ga–N stretch.^{27,30} Broad weak bands around 3200 and 2080 cm^{-1} are also observed. The former is presumably due to the N–H stretch.^{11,15,16} Kouvatakis and Beach assigned bands they observed at ≈ 2000 to Ga–H species.³⁰ We are reluctant to make the Ga–H assignment without having done the requisite labeling experiments because formation of Ga–H bonds from the precursors is unlikely.^{4,5}

Backscattering analyses (Fig. 5) suggest that the plasma and thermally deposited films are slightly nitrogen rich. Carbon peaks are observed in the spectra for some of the films with the carbon levels varying between 3 and 5 at. % (Table II). Peaks due to oxygen are absent in the spectra, however, suggesting oxygen contents of $< \text{few at. \%}$. Gallium nitride films deposited by APCVD from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 had N/Ga ratios of 1.05 to 1.5, depending on the deposition temperature.⁵

The plasma and thermally deposited GaN films have hydrogen contents between 13 and 27 at. % (Table II). In both deposition processes the hydrogen contents are lowest at the highest deposition temperatures. There appear to be no reports in the literature on the quantification of hydrogen in plasma-deposited gallium nitride films. APCVD films prepared from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 were reported to have 10–24 at. % hydrogen incorporation.⁵

Transmission spectra for films deposited by thermal CVD are shown in Fig. 6. The films are transparent in the visible and near-IR regions with the transmittances varying between 90% and 97% for the thermally deposited films. Similar results were obtained for plasma deposited films. Plots of d^2E^2 vs E gave optical band gaps varying between 3.2–4.8 eV for the plasma deposited films and 3.2–4.4 eV for the thermally deposited films. In general the band gaps increased with increasing deposition temperature for both the plasma and thermally deposited materials. APCVD GaN films deposited from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 had band gaps between 3.8 and 4.2 eV.⁵ The reported band gap for plasma

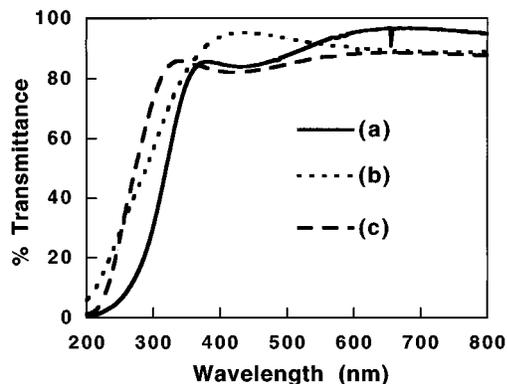


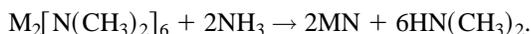
FIG. 6. Transmission spectra of gallium nitride films deposited by thermal CVD from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 at (a) 183, (b) 301, and (c) 389 °C on quartz.

gallium nitride films deposited from $\text{Ga}(\text{CH}_3)_3$ and NH_3 was 3.25 eV.²⁷ GaN films produced by electron cyclotron resonance plasma from gallium and N_2 had band gaps between 3.3–3.45 eV.²⁸ Single crystal gallium nitride has a band gap of 3.4 eV.²

Refractive indexes of the films are listed in Tables II. They varied between 2.1 and 2.4 for the plasma-deposited gallium nitride and between 1.8 and 2.0 for the thermally deposited material. GaN films prepared by APCVD from $\text{Ga}_2[\text{N}(\text{CH}_3)_2]_6$ and NH_3 had refractive indexes between 1.86 and 2.17 (Ref. 5) and those deposited by rf reactive sputtering of gallium in a nitrogen atmosphere had refractive indexes of 2.1–2.4.³¹

IV. DISCUSSION

The films produced in the thermal and plasma processes from the $\text{M}_2[\text{N}(\text{CH}_3)_2]_6$ compounds and ammonia are nearly stoichiometric with <5 at. % carbon contamination. Without the ammonia co-reactant, however, large amounts of carbon contamination were observed in the films. This suggests that in the thermal depositions the ammonia undergoes transamination reactions with the dimethylamido compounds, which displaces the dimethylamido ligands as dimethylamine and rid the precursor of carbon containing groups.^{4,5} Thus, the idealized chemical reaction to form the nitrides from the amido compounds can be written as



It is more difficult to say how the ammonia helps to minimize carbon contamination in the plasma process, but presumably the NH_x radical fragments function similarly to ammonia in the thermal process.

V. CONCLUSIONS

We have used hexakis(dimethylamido)dimetal complexes, $\text{M}_2[\text{N}(\text{CH}_3)_2]_6$ ($\text{M}=\text{Al}, \text{Ga}$), and ammonia to prepare nearly stoichiometric aluminum and gallium nitride thin films with and without plasma excitation at temperatures as low as 200 °C. Although the metal precursors have nitrogen con-

taining ligands, the ammonia co-reactant is necessary to minimize carbon contamination (<5 at. %). The growth rates of the plasma-deposited aluminum and gallium nitride films from the $\text{M}_2(\text{NMe}_2)_6/\text{NH}_3$ system were higher than for films produced by other plasma CVD techniques that use metal alkyls and ammonia or N_2H_4 as precursors. In particular, the AlN growth rate was as high as 1300 Å/min. The films were highly transparent in the visible and near-infrared region, and the aluminum nitride films displayed promising barrier properties in diffusion experiments for a Au/AlN/Si metallization scheme. Our results suggest that $\text{M}_2[\text{N}(\text{CH}_3)_2]_6$ ($\text{M}=\text{Al}, \text{Ga}$) are promising precursors for low temperature/low-pressure thermal and plasma-enhanced CVD of group III nitride thin films. A similar conclusion was reached regarding the attractiveness of tetrakis(dimethylamido)metal complexes $\text{M}[\text{N}(\text{CH}_3)_2]_4$ ($\text{M}=\text{Si}, \text{Ge}, \text{Sn}$) for depositing silicon, germanium, and tin nitride thin films by using the same method and apparatus described herein.⁷

ACKNOWLEDGMENTS

The authors are grateful to the State of Texas for financial support through the Texas Center for Superconductivity at the University of Houston. One author (D.M.H.) also acknowledges support from the Robert Welch Foundation and the Texas Advanced Research Program. He was a 1992–1994 Alfred P. Sloan Research Fellow. A second author (D.J.E.) acknowledges support from the Texas Advanced Technology Program.

- ¹L. M. Sheppard, *Ceram. Bull.* **69**, 1801 (1990).
- ²J. I. Pankove, *Mater. Res. Soc. Symp. Proc.* **162**, 515 (1990).
- ³I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu, and N. Sawaki, *J. Cryst. Growth* **98**, 209 (1989).
- ⁴R. G. Gordon, U. Riaz, and D. M. Hoffman, *J. Mater. Res.* **7**, 1679 (1992).
- ⁵R. G. Gordon, D. M. Hoffman, and U. Riaz, *Mater. Res. Soc. Symp. Proc.* **242**, 445 (1992).
- ⁶S. Strite, M. E. Lin, and H. Morkoç, *Thin Solid Films* **231**, 197 (1993).
- ⁷D. M. Hoffman, S. P. Rangarajan, S. D. Athavale, D. J. Economou, J. R. Liu, Z. S. Zheng, and W.-K. Chu, *J. Vac. Sci. Technol. A* **13**, 820 (1995).
- ⁸D. M. Hoffman, S. P. Rangarajan, S. D. Athavale, S. C. Deshmukh, D. J. Economou, J.-R. Liu, Z. Zheng, and W.-K. Chu, *J. Mater. Res.* **9**, 3019 (1994).
- ⁹K. M. Waggoner, M. M. Olmstead, and P. P. Power, *Polyhedron* **9**, 257 (1990).
- ¹⁰R. Jacobsson, *Thin Solid Films* **34**, 191 (1976).
- ¹¹L. V. Interrante, W. Lee, M. McConnell, N. Lewis, and E. Hall, *J. Electrochem. Soc.* **136**, 472 (1989).
- ¹²D. C. Boyd, R. T. Haasch, D. R. Mantell, R. K. Schulze, J. F. Evans, and W. L. Gladfelter, *Chem. Mater.* **1**, 119 (1989).
- ¹³M. David, S. V. Babu, and D. H. Rasmussen, *AIChE J.* **36**, 871 (1990).
- ¹⁴F. Hasegawa, T. Takahashi, K. Kubo, and Y. Nannichi, *Jpn. J. Appl. Phys.* **26**, 1555 (1987).
- ¹⁵M. J. Almond, C. E. Jenkins, and D. A. Rice, *J. Organomet. Chem.* **443**, 137 (1993).
- ¹⁶D. K. Gaskill, N. Bottka, and M. C. Lin, *J. Cryst. Growth* **77**, 418 (1986).
- ¹⁷H. Nomura, S. Meikle, Y. Nakanishi, and Y. Hatanaka, *J. Appl. Phys.* **69**, 990 (1991).
- ¹⁸S. Meikle, H. Nomura, Y. Nakanishi, and Y. Hatanaka, *J. Appl. Phys.* **67**, 483 (1990).

- ¹⁹W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).
- ²⁰Z. Zheng, J.-R. Liu, X. T. Cui, W.-K. Chu, S. P. Rangarajan, and D. M. Hoffman, *J. Mater. Res.* **10**, 3124 (1995).
- ²¹A. Turos and O. Meyer, *Nucl. Instrum. Methods Phys. Res. B* **4**, 92 (1984).
- ²²W. Baronian, *Mater. Res. Bull.* **7**, 119 (1972).
- ²³J. Bauer, L. Biste, and D. Bolze, *Phys. Status Solidi A* **39**, 173 (1977).
- ²⁴W. M. Yim, E. J. Stofko, P. J. Zanzucchi, J. I. Pankove, M. Ettenberg, and S. L. Gilbert, *J. Appl. Phys.* **44**, 292 (1973).
- ²⁵G. A. Cox, D. C. Cummins, K. Kawabe, and R. H. Tredgold, *J. Phys. Chem. Solids* **28**, 543 (1967).
- ²⁶J. N. Musher and R. G. Gordon, *J. Electron. Mater.* **20**, 1105 (1991).
- ²⁷S. W. Choi, K. J. Bachmann, and G. Lucovsky, *J. Mater. Res.* **8**, 847 (1993).
- ²⁸S. Zhang and D. E. Brodie, *Thin Solid Films* **237**, 124 (1994).
- ²⁹P. J. Born and D. S. Robertson, *J. Mater. Sci.* **15**, 3003 (1980).
- ³⁰J. Kouvetakis and D. B. Beach, *Chem. Mater.* **1**, 476 (1989).
- ³¹H. J. Hovel and J. J. Cuomo, *Appl. Phys. Lett.* **20**, 71 (1972).