Chem. Mater. **1991**, *3*, 1093-1097

Fourier Transform Infrared Spectroscopic Study of Predeposition Reactions in Metalloorganic Chemical Vapor Deposition of Gallium Nitride. 2

B. S. Sywe, J. R. Schlup, and J. H. Edgar*

Department of Chemical Engineering, Durland Hall, Kansas State University, Manhattan, Kansas 66506-5102

Received June 20, 1991. Revised Manuscript Received August 13, 1991

This is the second paper regarding the predeposition reactions that occur during metalloorganic chemical vapor deposition (MOCVD) of gallium nitride (GaN). Studies of the reactions between trimethylgallium (TMGa) and the nitrogen sources ammonia (NH_3) and nitrogen trifluoride (NF_3) have been reported previously. In the present work, triethylgallium (TEGa) was used as the Ga source, and reactions between TEGa and the nitrogen sources NH_3 and NF_3 were studied with Fourier transform infrared (FTIR) spectroscopy. Just as for the TMGa + NH_3 system, the reaction between TEGa and NH_3 went to completion immediately after mixing at room temperature. The resulting mixture of reactants and adduct, TEGa:NH_3, was observed in the gas phase via FTIR spectroscopy. Assignments of the IR absorption bands of gaseous TEGa:NH_3 were made. The room-temperature vapor pressure of TEGa:NH_3 is lower than that of TMGa:NH_3, which will inhibit transport of the Ga species to the deposition zone in MOCVD of GaN using TEGa as the Ga source. At 150 °C, chemical equilibrium was established between the gaseous adduct, TEGa:NH_3, and unreacted TEGa and NH_3. The forward rate constant of this predeposition reaction is 3.12×10^{-3} $Torr^{-1}$ s^{-1}, which is less than the value determined for TMGa + NH_3 (5.89×10^{-3} $Torr^{-1}$ s^{-1}). When either TMGa or TEGa was mixed with NF_3, no evidence of gas-phase adduct formation was observed at either room temperature or 150 °C.

Introduction

The room-temperature predeposition reaction is a problem commonly encountered in the metalloorganic chemical vapor deposition (MOCVD) of several compound semiconductors. The MOCVD process is typically accomplished by the reaction of metal alkyls with a hydride of the nonmetal component. These precursors are very susceptible to forming adducts, even at room temperature, because metal alkyls are Lewis acids and the hydrides of the nonmetal component are Lewis bases.[1] Predeposition reactions have been observed in many compound semiconductor systems,[2-8] as summarized in Table I. Formation of nonvolatile adducts makes reliable transport of the reactants to the deposition zone difficult; thus precise control of both the thickness and compositional uniformity of the epitaxial layer becomes problematic. Solutions to this problem include two coaxial delivery tubes (which keep the reactants separate until just before the substrate) with a high flow velocity,[2] low operating pressure,[9] or, more directly, alternative source materials which do not form adducts.

Gallium nitride (GaN) is a direct wide energy bandgap (3.45 eV) semiconductor with a high thermal conductivity (1.3 W/cm K).[10] Potential device applications include high-frequency power switching devices and short-wavelength optoelectronic devices.[11] Trimethylgallium (TMGa) is the most common Ga source in MOCVD of GaN, and triethylgallium (TEGa) is an alternative for TMGa. The potential advantage of TEGa over TMGa is reduced incorporation of carbon into the epitaxial layers.[12] For production applications, TMGa is more attractive because it possesses higher growth rates that are temperature independent over a wide temperature range.[12] Ammonia (NH_3) has long been used as the nitrogen source in MOCVD of nitride semiconductors, but it has two major problems. First, the uniformity of the deposited layer is poor because of the predeposition reactions between NH_3 and TMGa or TEGa at room temperature. Second, the deposition temperature is high (greater than 800 °C) as a consequence of the thermal stability of NH_3.[13] Thus, there have been numerous attempts to find alternative nitrogen sources[13-17] or single-source GaN precursors.[18-21]

Table I. Reported Predeposition Reactions in MOCVD of Compound Semiconductors

semiconductor	precursors[a]	ref
GaN	TMGa + NH_3 TEGa + NH_3	2, 3
AlN	TMA1 + NH_3	2
GaAs	TMGa + AsH_3	4
InP	TMIn + PH_3 TEIn + NH_3	5
InAs	TMIn + AsH_3 TEIn + AsH_3	6, 7
ZnS	DMZn + H_2S	8
ZnSe	DMZn + H_2Se	8

[a] Notation for metallorganics: TMGa (trimethylgallium), TEGa (triethylgallium), TMA1 (trimethylaluminum), TMIn (trimethylindium), TEIn (triethylindium), and DMZn (dimethylzinc).

---

* Author to whom correspondence should be addressed.

(1) Ludowise, M. J. *J. Appl. Phys.* **1985**, *58*, R31.

(2) Manasevit, H. M.; Erdmann, F. M.; Simpson, W. I. *J. Electrochem. Soc.* **1971**, *118*, 1864.

(3) Andrews, J. E.; Littlejohn, M. A. *J. Electrochem. Soc.* **1975**, *122*, 1273.

(4) Piocos, E. A.; Ault, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 8978.

(5) Gerrard, N. D.; Nicholas, D. J.; Willium, J. O.; Johns, A. C. *Chemtronics* **1988**, *3*, 17.

(6) Johnston, W. D., Jr.; DiGiuseppe, M. A.; Wilt, D. P. *AT&T Technical J.* **1989**, *Jan/Feb*, 53.

(7) Agnello, P. D.; Ghandhi, S. K. *Solar Cells* **1988**, *24*, 117.

(8) Wright, P. J.; Parbrook, P. J.; Cockayne, B.; Jones, A. C.; Orrell, E. D.; O'Donnell, K. P.; Henderson, B. *J. Cryst. Growth* **1989**, *94*, 441.

(9) Khan, M. A.; Skogman, R. A.; Schulze, R. G.; Gershenzon, M. *Appl. Phys. Lett.* **1983**, *42*, 430.

(10) Sichel, E. K.; Pankove, J. I. *J. Phys. Chem. Solids* **1977**, *38*, 330.

(11) Davis, R. F.; Sitar, Z.; Williams, B. E.; Kong, H. S.; Kim, H. J.; Palmour, J. W.; Edmond, J. A.; Ryu, J.; Glass, J. T.; Carter, C. H. Jr. *Mater. Sci. Eng.* **1988**, *B1*, 77.

(12) Brauers, A.; Weyers, M.; Balk, P. *Chemtronics* **1989**, *4*, 8.

(13) Gaskill, D. K.; Bottka, N.; Lin, M. C. *Appl. Phys. Lett.* **1986**, *48*, 1449.

(14) Gaskill, D. K.; Bottka, N.; Lin, M. C. *J. Cryst. Growth* **1986**, *77*, 418.

0897-4756/91/2803-1093$02.50/0

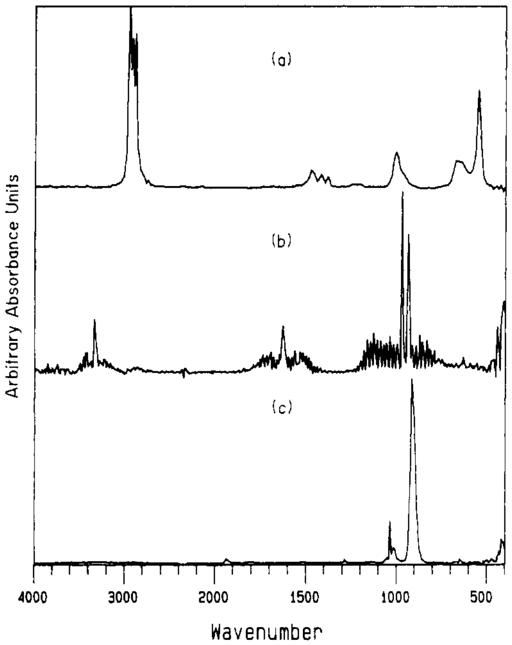

Figure 1. Infrared absorption spectrum of (a) TEGa, (b) NH_3, and (c) NF_3 at room temperature.

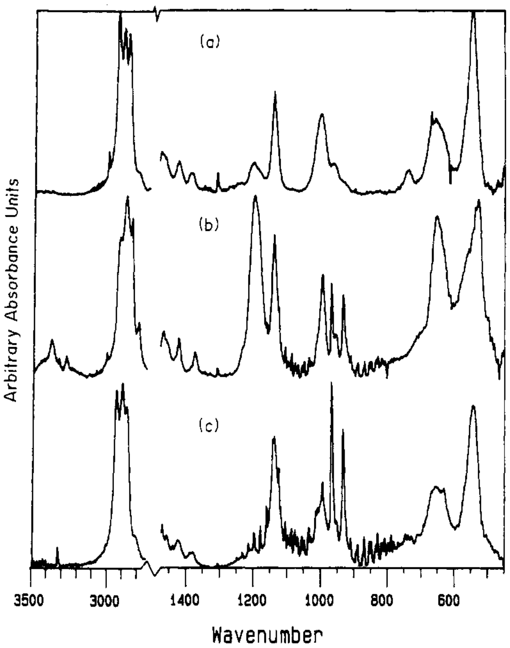

Figure 2. Infrared absorption spectra of (a) TEGa + NH_3 at room temperature with TEGa in excess, (b) TEGa + NH_3 at room temperature with NH_3 in excess, and (c) TEGa + NH_3 at 150 °C with NH_3 in excess.

One reactant reported to have a low deposition temperature (440 °C) is nitrogen trifluoride (NF_3),[17] which has a lower bond energy (277 kJ/mol) than NH_3 (391 kJ/mol). In addition, NF_3 is a nonpolar molecule with smaller dipole moment (0.234 D as compared with 1.42 D for NH_3),[22] which will help in reducing the extent of the predeposition reaction.

In the previous study using in situ Fourier transform infrared (FTIR) spectroscopy, it was confirmed that no reaction occurred between TMGa and NF_3 for temperatures up to 150 °C. TMGa reacted with NH_3 in the same temperature range and the resulting adduct, TMGa:NH_3, was detected in the gas phase via FTIR spectroscopy.[23] In the present work, the reactivity between TEGa and the nitrogen sources (NH_3 and NF_3) was studied using the same techniques.

Experimental Section

The reactions between TEGa and the nitrogen sources NH_3 and NF_3 were monitored in situ in an infrared gas transmission cell at room temperature and at 150 °C. Kinetic data at these two temperatures were obtained. The spectral region observed was 400–4000 cm^{-1} with resolution of 4 cm^{-1}. The gas cell was comprised of a main body and a small chamber, which were connected by a pneumatic valve. Before mixing, vapors of the reagents were loaded into the main body and the small chamber of the gas cell separately. Then the pneumatic value was triggered to allow mixing. The partial pressures of all components were less than 10 Torr, and no carrier gas was employed. In addition to the IR study, the vapor pressure of the resulting adduct at room temperature was estimated by mixing the reactants in a simple constant-volume reactor and recording the pressure change. This information can thus be used to derive the vapor pressure of the resulting adduct (assuming ideal gas behavior). Further details about the equipment and the procedures utilized have been described previously.[23]

Results and Discussions

The IR absorbance spectra of pure gaseous TEGa, NH_3, and NF_3 at room temperature are shown in Figure 1. The Ga–C asymmetric stretching of TEGa occurs at 543 cm^{-1} with strong intensity. Other peaks include three strong absorptions at 2951, 2917, and 2883 cm^{-1} in the C–H stretching region and three medium absorptions at 1471, 1418, and 1382 cm^{-1} in the CH_3 deformation region. The medium peaks at 1001 and 640 cm^{-1} are attributed to CH_2 twisting and rocking, respectively.[24] NH_3 has absorptions at 3333, 1625, 965, and 931 cm^{-1} corresponding to N–H symmetric stretching, asymmetric bending, and symmetric bending modes (965 and 931 cm^{-1}), respectively.[25] The vibrational–rotational structure is easily seen in NH_3 spectrum, even at 4-cm^{-1} resolution. NF_3 has strong absorptions at 1031 and 909 cm^{-1}, which correspond to N–F stretching and deformation modes.[22] The Ga–C peak of TEGa at 543 cm^{-1} and the intense peaks at 965 and 909 cm^{-1} for NH_3 and NF_3, respectively, were selected as the peaks for use in quantitative analysis.

Figure 2 shows the IR absorption spectra of (a) TEGa + NH_3 at room temperature with TEGa in excess, (b) TEGa + NH_3 at room temperature with NH_3 in excess, and (c) TEGa + NH_3 at 150 °C with NH_3 in excess. In the room-temperature spectrum with TEGa in excess (Figure 2a), none of the NH_3 peaks were observed. The disappearance of the NH_3 peaks indicates that the reaction between TEGa and NH_3 is complete at room temperature.

---

(15) Mizuta, M.; Fujieda, S.; Matsumoto, Y.; Kawamura, T. *Jpn. J. Appl. Phys.* **1986**, *25*, L945.

(16) Fujieda, S.; Mizuta, M.; Matsumoto, Y. *Jpn. J. Appl. Phys.* **1987**, *26*, 2067.

(17) Furukawa, Y. *Jpn. J. Appl. Phys.* **1984**, *23*, 376.

(18) Kouvetakis, J.; Beach, D. B. *Chem. Mater.* **1989**, *1*, 476.

(19) Gladfelter, W. L.; Hwang, J.-W.; Phillips, E. C.; Evans, J. F.; Hanson, S. A.; Jensen, K. F. *Mater. Res. Soc. Symp. Proc.* **1991**, *204*, 83.

(20) Gordon, R. G.; Hoffman, D. M.; Riaz, U. *Mater. Res. Soc. Symp. Proc.* **1991**, *204*, 95.

(21) Ho, K.-L.; Jensen, K. F.; Hwang, J.-W.; Evans, J. F.; Galdfelter, W. L. *Mater. Res. Soc. Symp. Proc.* **1991**, *204*, 101.

(22) Emeleus, H. J.; Shreeve, J. M.; Verma, R. D. *The Nitrogen Fluorides and Some Related Compounds*; *Advances in Inorganic Chemistry*; Sykes, A. G., Ed.; Academic Press: San Diego, 1989; Vol. 33, pp 139–196.

(23) Sywe, B. S.; Schlup, J. R.; Edgar, J. H. *Chem. Mater.* **1991**, *3*, 737.

(24) Kurbakova, A. P.; Leimes, L. A.; Aleksnyan, V. T.; Golubinskaya, L. M.; Zorina, E. N.; Bregadze, V. I. *Zh. Strukt. Khim.* **1974**, *15*, 1083.

(25) Tripathi, A.; Mazzarese, D.; Conner, W. C. *J. Electron. Mater.* **1989**, *18*, 45.

Table II. Frequencies of the Normal Vibrations of NH_3, TEGa, and TEGa:NH_3, cm^{-1}

NH_3(g)	TEGa(g)	TEGa:NH_3(g)	assignment[a]
3432 vw[b]			NH_3 a str
3414 vw		3381 w	
3333 w		3285 w	NH_3 s str
	2953 vs	2931 vs	CH_3 str
	2916 vs	2893 vs	CH_3 str
	2881 vs	2856 vs	CH_3 str
	2746 sh	2808 sh	CH_2 str
1625 w		1605 w	NH_3 a def
	1471 w	1464 w	CH_3 def
	1418 w	1419 w	CH_2 def
	1382 w	1371 w	CH_3 def
	1001 s	1194 s	CH_3 rock and CH_2 twist
965 m		992 m	NH_3 s def
931 m		952 m	
	640 m	650 s	CH_2 rock
	543 s	526 s	Ga–C str

[a] Abbreviations for peak assignment: a = asymmetric, s = symmetric, str = stretching, def = deformation. [b] Abbreviations for relative peak intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

If any product, TEGa:NH_3, is present in the gas phase, its spectrum would be superimposed into the spectrum of the remaining TEGa. This is indeed the case, although it is difficult to tell from Figure 2a alone.

When NH_3 is in excess at room temperature, the resulting spectrum (Figure 2b) becomes a superposition of the spectra of NH_3 and TEGa:NH_3 since the limiting reactant, TEGa, is totally consumed. Since the NH_3 peaks can be identified clearly in this spectrum, the remaining peaks are assigned to gaseous TEGa:NH_3. Since the formation of TEGa:NH_3 does not destroy any chemical bond, assignments of the gas-phase TEGa:NH_3 absorptions can be made on the basis of the TEGa and NH_3 absorptions. First, the two peaks at 3381 and 3285 cm^{-1} in the N–H stretching region correspond to the NH_3 peaks at 3414 and 3333 cm^{-1}. Second, three strong peaks appear at 2931, 2893, and 2856 cm^{-1} in the C–H stretching region corresponding to the TEGa peaks at 2953, 2916, and 2881 cm^{-1}. Third, a weak peak is observed at 1605 cm^{-1} corresponding to the NH_3 peak at 1625 cm^{-1}. Fourth, the three peaks at 1464, 1419, and 1371 cm^{-1} are the counterparts of the three C–H deformation peaks in TEGa at 1471, 1418, and 1381 cm^{-1}. Fifth, the strong peak at 1194 cm^{-1} corresponds to the C–H rocking peak in TEGa at 1001 cm^{-1}. Sixth, there are two peaks at 992 and 952 cm^{-1}, corresponding to the NH_3 peaks at 965 and 931 cm^{-1}. Finally, two peaks appear at 650 and 526 cm^{-1} corresponding to the TEGa peaks at 640 and 543 cm^{-1}. The peak at 526 cm^{-1} is associated with the Ga–C stretching for TEGa:NH_3. These results are summarized in Table II. It is noticed that the Ga–C stretching frequency decreases from TMGa (583 cm^{-1}) to TMGa:NH_3 (559 cm^{-1}),[23] to TEGa (543 cm^{-1}), to TEGa:NH_3 (526 cm^{-1}), suggesting a decreasing trend in the Ga–C bond strength.

Figure 2c shows the spectrum of TEGa + NH_3 at 150 °C with NH_3 in excess. In this spectrum, both TEGa and NH_3 absorptions are observed. Quantitative analysis indicates that equal amounts of TEGa and NH_3 were consumed, but neither of the reactants was exhausted. Therefore, at 150 °C, adduct formation reached equilibrium prior to complete conversion of the reactants. Because of the strong absorbances of TEGa, no specific TEGa:NH_3 peaks were identified. However, subtle changes in the peak shape can be observed. For example, the relative intensities of the three C–H stretching peaks in the region 2800–3100 cm^{-1} are different from the corresponding peaks in the pure TEGa spectrum; this is due to the superposition of the corresponding TEGa:NH_3 peaks in the same region.

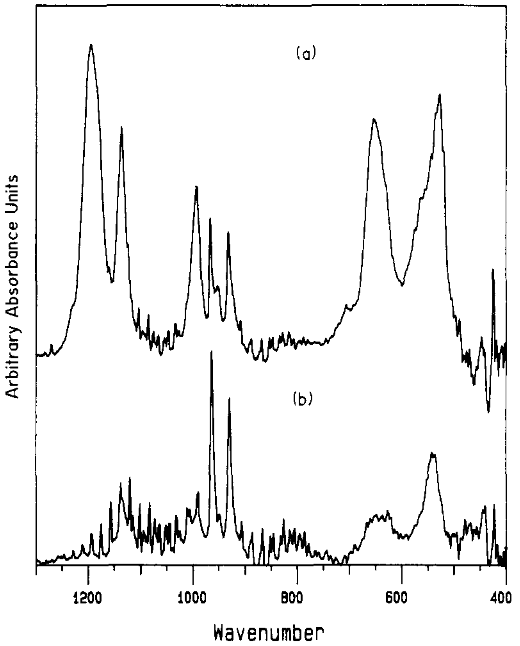

Figure 3. Infrared absorption spectra of TEGa + NH_3 (with NH_3 in excess), upon heating from (a) room temperature to (b) 150 °C.

In the spectrum of TEGa + NH_3 at 150 °C, a peak at 1136 cm^{-1} is also present. This peak appears in every mixture spectrum of TEGa and NH_3. In the room-temperature spectrum with NH_3 in excess (Figure 2b), the intensity of this peak is less than that of the TEGa:NH_3 peak at 1194 cm^{-1}. In other spectra of TEGa + NH_3 (Figure 2a,c), the TEGa:NH_3 peak at 1194 cm^{-1} and all other TEGa:NH_3 peaks do not appear, but the peak 1136 cm^{-1} is observed. Therefore, it can be concluded that this peak does not come from the adduct TEGa:NH_3. Since the gaseous TMGa:NH_3 has a peak at the same frequency,[23] a possible explanation is it comes from the adduct TMGa:NH_3 which is produced from NH_3 and the residual TMGa adsorbed on the cell surface from previous experiments.

In another experiment, a room-temperature mixture of TEGa and NH_3 was heated to 150 °C. The spectra taken at room temperature and at 150 °C are shown in parts a and b of Figure 3, respectively. The appearance of the 1136-cm^{-1} peak indicates some residual TMGa:NH_3 is present. Upon heating to 150 °C, the NH_3 peaks at 965 and 931 cm^{-1} became stronger. The TEGa peaks reappear and the TEGa:NH_3 peaks become unobservable. Therefore, dissociation of the TEGa:NH_3 molecules has occurred. Apparently, chemical equilibrium between the gaseous product TEGa:NH_3 and the reactants TEGa and NH_3 has a smaller equilibrium constant at 150 °C than at room temperature.

In a similar experiment in which a mixture of TEGa + NH_3 at room temperature was heated, a spectrum was taken 5 min after power was applied to the heating tape that was wound on the gas cell surface. Surprisingly, a spectrum of TEGa:NH_3 was more than 6 times as intense as the room-temperature spectrum. This spectrum is overlaid on the room-temperature spectrum in Figure 4 on the same scale. The sudden increase in the absorbance of TEGa:NH_3 is ascribed to the vaporization of the condensed TEGa:NH_3 upon heating. This spectrum in Figure 4b was obtained immediately after the condensed TEGa:NH_3 molecules were vaporized and before dissoci-

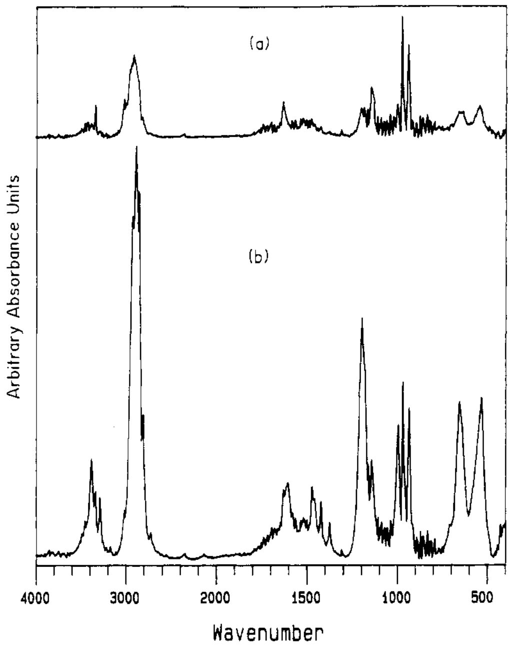

Figure 4. Infrared absorption spectra of (a) condensed TEGa:NH_3 and (b) vaporized TEGa:NH_3 in mixture of TEGa + NH_3.

ation of these molecules occurred. The spectrum also shows a small increase in the NH_3 peaks at 965 and 931 cm^{-1}, but no increase in the peak at 1136 cm^{-1}. These data indicate that most of the TEGa:NH_3 molecules are condensed at room temperature. The additional intensity facilities observing and assigning the TEGa:NH_3 peaks.

Similar to the TMGa + NH_3 system,[23] kinetic data of room-temperature experiments between TEGa and NH_3 could not be obtained because the reactions essentially were complete upon mixing. Using an analog plotter to monitor changes in cell pressure with time, it was estimated that the room-temperature formation of TEGa:NH_3 was complete in less than 0.2 s.

In the 150 °C experiments, spectra taken at intervals after mixing showed a continuous decrease in the peak intensities of TEGa and NH_3. The reaction reached chemical equilibrium in about 4 min. The predeposition reaction between TEGa and NH_3 is assumed to be a reversible bimolecular reaction:

$$\mathrm{TEGa(g)} + \mathrm{NH_3(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{TEGa{:}NH_3(g)} \qquad (1)$$

Assuming no product is present initially, the integrated rate equation below can be derived relating the conversion of NH_3, X_A, and time, t:

$$\ln\left[\frac{X_A - P_{B0}/(P_{A0}X_{Ae})}{X_A - X_{Ae}}\right] = \ln\left[\frac{P_{B0}}{P_{A0}X_{Ae}^2}\right] + (P_{B0}/X_{Ae} - P_{A0}X_{Ae})k_1 t \qquad (2)$$

where $X_A = (P_{A0} - P_A)/P_{A0}$ is the conversion of NH_3 at time t, X_{Ae} is the conversion of NH_3 at equilibrium, P_{A0} is the initial concentration of NH_3 in Torr, P_{B0} is the initial concentration of TEGa in Torr, k_1 is the rate constant for the forward reaction in $Torr^{-1}$ s^{-1}, and t is the reaction time in seconds.

By plotting the logarithmic term of the left-hand side of eq 2 vs time (Figure 5), a straight line should be obtained with a slope equal to the forward rate constant k_1 times the constant term in the parentheses in the right hand side.

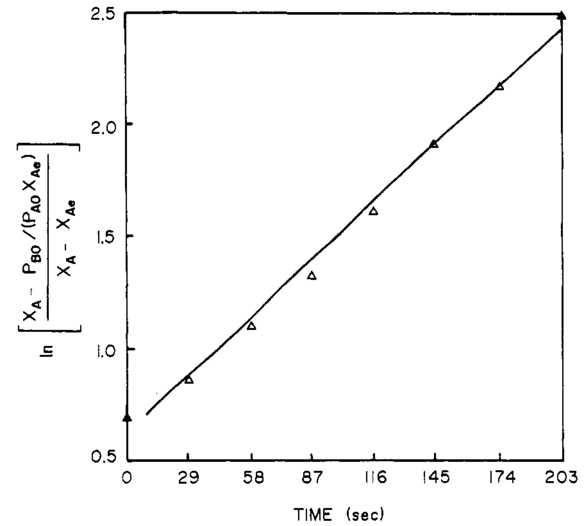

Figure 5. Kinetic data for TEGa + NH_3 at 150 °C.

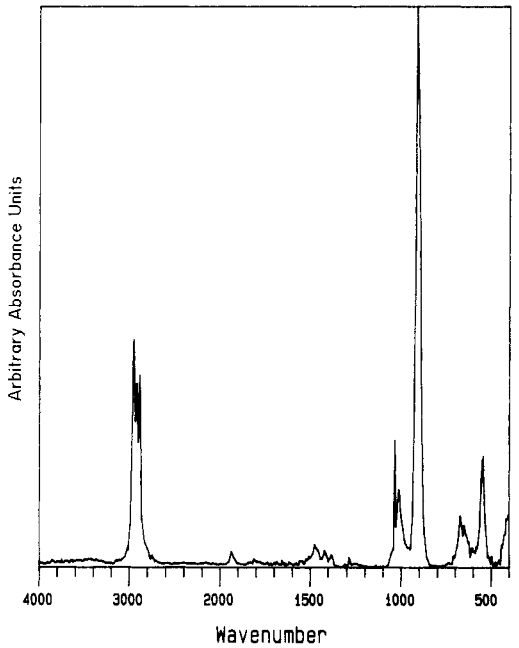

Figure 6. Infrared absorption spectra of TEGa + NF_3 at room temperature.

The forward rate constant measured for TEGa + NH_3 at 150 °C is 3.12 × 10^{-3} $Torr^{-1}$ s^{-1}. This is smaller than that determined for TMGa + NH_3 system at same temperature (5.89 × 10^{-3} $Torr^{-1}$ s^{-1}).

Figure 6 shows the spectrum of TEGa + NF_3 at room temperature. This spectrum is identical with the superposition of pure component spectra. The spectrum of TEGa + NF_3 at 150 °C is identical with the spectrum in Figure 6. The intensities of NF_3 peaks in both systems remain unchanged for 20 min following mixing of the gases. Therefore, adduct formation did not occur at either temperature.

FTIR spectroscopic results indicate both TMGa and TEGa react with NH_3 at room temperature to form TMGa:NH_3 and TEGa:NH_3, respectively. The weak IR absorption of these adducts suggests only a small portion of these adducts remain in the gas phase; most of the product condenses onto reactor surfaces. A vapor pressure of 0.92 Torr for TMGa:NH_3 at room temperature had been measured previously.[23] In the TEGa + NH_3 system, the vapor pressure of TEGa:NH_3 was extremely low; thus it could not be measured with the current experimental setup. This result indicates almost all the reaction product, TEGa:NH_3, is in a condensed phase. The difference in the volatilities of TMGa:NH_3 and TEGa:NH_3 is important. At room temperature, TMGa:NH_3 is more volatile than TEGa:NH_3. In MOCVD of GaN with a cold-wall reactor, using TMGa is beneficial because more Ga carrying species would reach the reaction zone. If TEGa were selected, most of TEGa would condense as TEGa:NH_3 before reaching the reaction zone. Adducts resulting from predeposition reactions during MOCVD of compound semiconductors probably would have higher vapor pressures when metalorganics with small alkyl groups (methyl instead of ethyl) are utilized. Thus, in considering the growth efficiency, the metallorganics with small alkyl groups would be favored as the presursors. For example, in MOCVD of GaAs using TMGa and AsH_3, the reported growth efficiencies vary from 1.8×10^3 to 1.5×10^4 μm/mol of TMGa. When TEGa was used, the growth efficiency was on the order of 10^2 μm/mol of TEGa.[26] In MOCVD of InP using TMIn and PH_3, a typical value of the growth efficiency was 6.9×10^3 μm/mol of TMIn. When TEIn was used, the growth efficiency dropped to a range of 4.5×10^2–3.8×10^3 μm/mol of TEIn.[26]

To eliminate the condensation of predeposition adduct in the MOCVD process, one possible solution is to use a hot-wall reactor instead of a cold-wall reactor. For example, wall temperatures set at about 150 °C would reduce the predeposition reaction and increase the vapor pressure of any adduct formed. Certainly, the optimal temperature will have to be determined experimentally. It must be much lower than the growth temperature in order to prevent premature deposition on the reactor walls.

From the aspect of limiting predeposition reactions, NF_3 is a good alternative nitrogen source since no evidence was obtained that predeposition reactions occurred between NF_3 and TMGa or TEGa. However, fluorine has a higher chemical activity than nitrogen; thus, fluorine-containing byproducts may be formed in addition to the growth of the nitride semiconductor. For example, in MOCVD of AlN with TMAl and NF_3 as the source materials, aluminum trifluoride (AlF_3) has been detected in the AlN films.[27]

Conclusions

The room-temperature predeposition reaction between the Ga source (TMGa or TEGa) and NH_3 is complete in less than 0.2 s following mixing. The resulting adduct TMGa:NH_3 had a vapor pressure of 0.92 Torr, while the vapor pressure of TEGa:NH_3 was lower. With FTIR spectroscopy, absorption spectra of gaseous TMGa:NH_3 and TEGa:NH_3 were observed, and the assignments of vibrational frequencies were given. Since no chemical bond was destroyed when adducts were formed, the correspondences between the adduct spectrum and the single-component spectra were evident. When TMGa or TEGa was mixed with NH_3 at 150 °C, chemical equilibrium was reached between the gaseous adduct (TMGa:NH_3 or TEGa:NH_3) and the reactants. By assuming a reversible bimolecular reaction, a forward rate constant of 5.89×10^{-3} $Torr^{-1}$ s^{-1} was measured for the predeposition reaction between TMGa and NH_3. For TEGa + NH_3 system, the forward rate constant at 150 °C is 3.12×10^{-3} $Torr^{-1}$ s^{-1}. With NF_3 as the nitrogen source, no evidence of adduct formation was observed with TMGa or TEGa at either room temperature or 150 °C. Therefore, NF_3 could be used as an alternative source of nitrogen in order to limit predeposition reactions.

Acknowledgment. This research is sponsored in part by a subcontract from the University of Florida (Grant No. MDA972-88-J-1006) and the Engineering Experiment Station at Kansas State University. Their support is gratefully acknowledged.

Registry No. TMGa, 1445-79-0; TEGa, 1115-99-7; GaN, 25617-97-4.

---

[26] Stringfellow, G. B. *Organometallic Vapor-Phase Epitaxy: Theory and Practice*; Academic Press: San Diego, CA, 1989; pp 10–11.

[27] Edgar, J. H.; Yu, Z. J.; Ahmed, A. U.; Rys, A. *Thin Solid Films* **1990**, *189*, L11.

Ligand Exchange in Adducts of Ethylaluminum Hydrides

Dario M. Frigo* and Piet J. Reuvers
Billiton Research B.V., Postbox 40, 6800 AA Arnhem, The Netherlands
Donald C. Bradley* and Halina Chudzynska
Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK
Harry A. Meinema,* Johanna G. Kraaijkamp, and Klaas Timmer
Department of Chemistry, TNO, Postbox 108, 3700 AC Zeist, The Netherlands

Received June 26, 1991. Revised Manuscript Received August 26, 1991

The compounds $EtAlH_2{\cdot}NMe_3$ and $Et_2AlH{\cdot}NMe_3$ have been shown by ^1H NMR spectroscopy to be fluxional mixtures of all species $Et_xAlH_{3-x}{\cdot}NMe_3$ ($x = 0$–3) in aromatic solvents. The pure liquids have also been shown to be mixtures by their volatilization behavior, and the tendency for $EtAlH_2{\cdot}NMe_3$ to separate at low temperatures into a solid plus a liquid, each of which has a different composition. This has potentially dire consequences for the usefulness of both of these compounds as precursors for the MOCVD of aluminum-containing layers.

Introduction

Metalloorganic chemical vapor deposition (MOCVD) is a technique whereby thin films of certain substances may be deposited on substrate materials by the chemical reaction of volatile metalloorganic precursors which are transported to the substrate via the vapor phase.[1] It has become an increasingly important process for a variety of applications, including the fabrication of microelectronic

---

[1] Manasevit, H. M. *Appl. Phys. Lett.* **1968**, *12*, 156.

0897-4756/91/2803-1097$02.50/0