

Preparation and Properties of Alane Dimethylethylamine, a Liquid Precursor for MOCVD

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The properties of $\text{AlH}_3 \cdot \text{NMe}_2\text{Et}$, DMEAl, have been examined particularly with respect to use as a precursor for the metalorganic chemical vapor deposition (MOCVD) of aluminum-containing layers. An optimal synthesis of DMEAl not involving ether solvents is also described. At ambient temperatures DMEAl is a colorless volatile liquid but has limited thermal stability, slowly decomposing to generate potentially high pressures of hydrogen. No dissociation of the adduct was observed in the infrared spectrum of the vapor at room temperature, but DMEAl does undergo some degree of dissociation during distillation in vacuo, thereby leaving a residue of involatile AlH_3 . Analysis by differential scanning calorimetry showed that DMEAl should not decompose explosively at elevated temperatures. It does not spontaneously inflame in air unless dropped onto vermiculite. The ^1H NMR spectrum is highly dependent upon concentration.

Introduction

Metalorganic chemical vapor deposition (MOCVD) is a technique whereby thin films are deposited on substrate materials by the chemical reaction of volatile precursors which are transported to the substrate via the vapor phase. It has become increasingly important for a variety of applications, including the fabrication of microelectronic devices, where it has been used to deposit the semiconducting,¹ insulating,² and metallization layers.³

MOCVD of aluminum layers for metallization has been achieved largely using Al trialkyls (R_3Al) as precursor; principally $\text{R} = i\text{-Bu}$ ⁴ but also $\text{R} = \text{Me}$.⁵ MOCVD of epitaxial layers of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and related semiconductors—also known as metalorganic vapor-phase epitaxy (MOVPE)—has been achieved mainly using Me_3Al as the source of aluminum.¹ However, there has been recent concern about these standard precursors: $(i\text{-Bu})_3\text{Al}$ has a tendency to decompose to the less volatile $(i\text{-Bu})_2\text{AlH}$ in the vapor lines to the reactor⁶ and frequently gives aluminum that is not conformal;⁴ use of Me_3Al for either aluminum or $\text{Al}_x\text{Ga}_{1-x}\text{As}$ leads to levels of carbon in the resulting layers that are unacceptably high for some applications.⁷

For MOVPE and $\text{Al}_x\text{Ga}_{1-x}\text{As}$, some authors have found that carbon incorporation was substantially reduced using group III precursors containing only ethyl ligands, i.e., Et_3Al and Et_3Ga .^{8,9} However, the very low vapor pressure

of Et_3Al (0.025 mbar at 20 °C¹⁰) resulted in low growth rates, and its lower thermal stability tended to give worse thickness and compositional uniformity over a substrate wafer.⁹ Others have found that Me_2AlH represented a substantial improvement over $(i\text{-Bu})_3\text{Al}$ or Me_3Al for the deposition of Al,¹¹ but this precursor appears to offer no advantages for $\text{Al}_x\text{Ga}_{1-x}\text{As}$.¹²

In addition, adducts between alane, AlH_3 , and tertiary amines were used as precursors for the deposition of Al over 20 years ago¹³ and have recently been used as precursors for MOCVD of Al^{14-18} and for both the MOVPE¹⁹⁻²¹ and chemical beam epitaxy (CBE)²² of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. The main advantage of such precursors is that they contain no carbon directly bonded to the metal; the tertiary amine ligands are so thermally robust that even under the conditions of MOCVD/MOVPE or CBE they are unlikely to be sources of carbon contamination.²³ Use of alane compounds should also reduce the tendency

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to incorporate oxygen into the growing layers because they form involatile species upon reaction with traces of oxygen or water,²⁴ whereas the trialkyls tend to form relatively volatile alkoxides (R₃AlOR)_n.²⁵

Trimethylamine alane AlH₃·NMe₃ (TMAAl) has been used with arsine and either Me₃Ga¹⁹ or Et₃Ga²⁰ for the MOVPE of Al_xGa_{1-x}As; the combination with Et₃Ga has also been used in CBE.²² On the basis of the carbon-related emissions in the low-temperature photoluminescence spectra (PL), levels of carbon in Al_xGa_{1-x}As layers grown by MOVPE using TMAAl, Me₃Ga and arsine were comparable with those using Me₃Al as the aluminum precursor. In contrast, replacement of Me₃Ga by Et₃Ga produced a significant reduction in carbon levels. This has been ascribed to gas-phase prereaction between the group III precursors whereby the alkyl ligands on the gallium are exchanged with the hydrides on the aluminum.²⁶ If this results in the formation of Al–Me species, then the carbon incorporation is likely to be as great as with Me₃Al. A further consequence of the prereaction is the observation of deposition on the reactor walls prior to the substrate, ascribed to decomposition of the rather unstable Ga–H species. Hitherto this problem has been overcome by reducing the reactor pressure and increasing the linear gas velocities.

Another problem with most of the alane adducts is their relatively low thermal stability,²⁷ which could compromise their practicability both with respect to safety and long-term storage. The thermal instability of the alane adducts, coupled to their relatively high melting points [77–78 °C for TMAAl; 95 °C for the analogous 1:2 adduct AlH₃·(NMe₃)₂],²⁷ necessitates evaporation from solid sources, the dosimetry of which is notoriously unreliable.²⁸ Several effects have been described to explain this variability in the rate of evaporation. Perhaps paramount is the tendency for the average crystal size in the sample to increase with time, thereby minimizing the surface free energy but, more significantly, decreasing the surface area from which evaporation takes place.²⁹ Other effects are more likely to arise if a carrier gas is used to entrain the precursor vapors: formation of voids in the solid sample through which the gas can pass with only minimal contact with the precursor,³⁰ and contamination of the surface of the solid to form a skin (e.g., of oxide) that obstructs evaporation. A gradual reduction in evaporation efficiency has been reported recently for TMAAl.³¹

Variations in precursor dosimetry for both MOCVD and CBE give similar uncertainties in the rates of deposition obtained and severely hinder accurate control of the composition of ternary and quaternary materials. For this reason, replacements for TMAAl (and the corresponding 1:2 adduct) that are liquids at ambient temperature have been sought. Indeed, deposition of Al has recently been reported using the precursor AlH₃·NEt₃,³² which melts at 19 °C²⁷ and can, therefore, be evaporated from the liquid

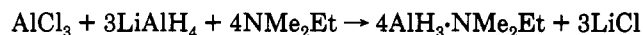
at ambient temperature. However, this compound is very unstable, decomposing above 40 °C,²⁷ and so the long-term stability of its output as a source in MOCVD or CBE is questionable.

We have recently reported the MOVPE of Al_xGa_{1-x}As using adducts involving the amine NMe₂Et.^{33,34} Some layers showed no detectable carbon-related signal in the 4.2 K PL spectrum even under extreme sensitivity, from which it was concluded that the levels of carbon were around 3 orders of magnitude lower than those grown with conventional precursors. In addition, there was clear evidence from the sharpness of the PL excitonic emissions that the dosimetry was markedly superior to that grown using the analogous solid TMAAl; indeed it was equal to that obtained from standard precursors, Me₃Al or Et₃Al.

We now describe the properties of the 1:1 adduct between alane and NMe₂Et, DMEAl, with specific reference to its use as a precursor for MOCVD/MOVPE and CBE. Also described is an optimal synthesis for DMEAl that involves no ether solvents, thus eliminating the chance of contamination of the precursor by a potential source of oxygen. DMEAl has also been used for the MOCVD of Al metal³⁵ and AlAs.³⁶

Preparation, Physical Properties, and Analysis

Hitherto, the amine adducts of alane have been prepared almost invariably by routes in which ethers were used as solvent. This is very likely to give contamination of the end product by the ether, which could lead to incorporation of oxygen in the Al-containing layers. Our synthesis uses only alkane solvents, which are inert in the deposition processes, and are volatile enough to effect easy separation from the product. A stoichiometric amount of the amine is added slowly to a slurry of LiAlH₄, AlCl₃, and pentane. The Al compounds are insoluble in the pentane and do not react at a measurable rate. However, upon addition of amine small amounts of these solids dissolve and then react with one another:



The alane “removes” the amine from the system by formation of an adduct and thus limits the extent of reaction to the amount of amine that has been added. Therefore, the exothermic reaction proceeds at the rate of addition of the amine (limited by the smooth reflux of the pentane). All byproducts are essentially insoluble in pentane, and so filtration gives efficient separation, and the product can be crystallized directly by cooling the filtrate. Purification by crystallization gives a product with a well-defined adduct ratio and avoids the partial dissociation that occurs upon distillation in vacuo (vide infra). This could be a useful synthesis for other alane adducts.

Samples were thus prepared in which the only trace impurities were as follows: Si, 0.2 ppm; Fe, 1 ppm. The level of iron was thought to be a potential problem if the

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Table 1. ^1H NMR Spectra of DMEAl and NMe_2Et versus Mole Fraction^a

compd	mole fraction	$\delta(\text{CH}_2\text{-CH}_3)^b$	$\delta(\text{N-CH}_3)^c$	$\delta(\text{N-CH}_2)^d$	$\delta(\text{Al-H})^e$	fwhm of (AlH), Hz
DMEAl	0.45	0.90	2.08	2.43	3.55	9
	0.21	0.83	1.99	2.33	3.82	14
	0.10	0.77	1.93	2.27	3.98	26
	0.04	0.73	1.87	2.21	4.10	66
NMe_2Et	0.42	0.93	2.04	2.14		
	0.22	0.95	2.06	2.15		

^a Recorded in C_6D_6 at 200 MHz; δ values quoted in ppm relative to Me_4Si . ^b Triplet, $J = 7.3$ Hz. ^c Sharp singlet. ^d Quartet, $J = 7.3$ Hz. ^e Broad singlet.

precursor were used for MOCVD or CBE or III-V semiconductors. It appears to be a contaminant in the AlCl_3 and could be removed by initial purification (e.g., by sublimation). However, no iron was found in samples of DMEAl that had undergone simple distillation in vacuo, from which it can be concluded that the iron species is of such low volatility that it will not be transported to the substrate during deposition. This is further borne out by the very good electrical and optical properties of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers that have been grown with the precursor.^{33,34}

At ambient temperatures DMEAl is a crystal-clear colorless liquid with melting point 5 °C; its density at 25 °C is 0.78 g/cm³, as compared with 0.68 g/cm³ at 20 °C for the free amine. Its viscosity has not been measured but appears to be comparable with that of Me_3Al . At room temperature it is only moderately soluble in pentane or hexane but readily dissolves upon mild heating. As with the analogous solid alane adducts $\text{AlH}_3\cdot\text{NMe}_3$ (TMAAl) and $\text{AlH}_3\cdot(\text{NMe}_3)_2$, DMEAl is decomposed very rapidly upon exposure to the atmosphere (see Stability).

The melting point of DMEAl is substantially lower than that of the analogous adduct with NMe_3 or NEt_3 .²⁷ This is probably due to the lower symmetry of the resulting adduct molecule using an asymmetrically substituted amine ligand as compared with the NMe_3 or NEt_3 adducts. This reduction in symmetry means that the molecules do not pack so readily into the crystal, and the structure is more easily disrupted by thermal vibrations. In addition, many highly symmetrical molecules are able to rotate without significant disruption of their crystal structure, thereby populating rotation states without actually melting. The symmetry effect is readily illustrated by the unusually high melting point of highly symmetric benzene relative to its substituted derivatives.³⁷ More pertinent illustrations of this effect are seen by the trends in the melting points of adducts of trimethylindium with the following tertiary amines and phosphines: NMe_3 , 67 °C; NMe_2Et , 62 °C; NMeEt_2 , 67 °C; NEt_3 , 94 °C; and PMe_3 , 47 °C; PMe_2Et , -13 °C; PMeEt_2 , <-25 °C; PEt_3 , 35 °C. For each adduct, a minimum in the melting point occurs with the asymmetrically substituted pnictides.³⁸

An alternative manner of introducing asymmetry into alane adducts to lower the melting point is to substitute some of the hydride ligands on the metal by alkyls. Indeed MOVPE of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has been achieved¹² using $\text{Et}_2\text{-AlH}\cdot\text{NMe}_3$, which is a liquid at ambient temperature.²⁷ Unfortunately, it has been shown that this liquid is not a discrete compound but an equilibrium mixture of $\text{Et}_3\text{-Al}\cdot\text{NMe}_3$, $\text{Et}_2\text{AlH}\cdot\text{NMe}_3$, $\text{EtAlH}_2\cdot\text{NMe}_3$, and $\text{AlH}_3\cdot\text{NMe}_3$ owing to rapid exchange of ligands on the metal. Upon vaporization at temperatures in the range 0–20 °C, the vapor is richer in the more volatile species (those containing more Al–H bonds) than is the liquid; the composition of the liquid gradually changes, and there is a concomitant

reduction in the vapor pressure of the source.³⁹ A similar effect has been observed with Me_2EtIn , Me_2EtAl , and their adducts with Lewis bases,⁴⁰ with MeEtCd ,⁴¹ and with mixtures consisting of $\text{Me}_x\text{Et}_{4-x}\text{Pb}$.⁴² In contrast, there is no evidence for ligand exchange in the amine NMe_2Et or its adducts with AlH_3 . This is expected in view of the enormous strength of the N–C bond in comparison with M–C or M–H bonds for the metals mentioned above.³⁷

The ^1H NMR spectrum of DMEAl in C_6D_6 shows the expected signals for the NMe_2Et moiety: singlets for the methyl ligands and a triplet plus quartet for the ethyl. However, the singlet due to Al–H is broad, presumably due to coupling to the ^{27}Al nucleus. The NMR data versus mole fraction are shown in Table 1 together with those for the free amine. In DMEAl the signals for the amine shift upfield with decreased mole fraction, whereas the alane signal moves downfield; the alane peak also becomes much broader. All CH_3 signals on the amine in DMEAl are upfield of those of the uncoordinated ligand, whereas the CH_2 moves from relatively deshielded to relatively shielded with decreasing concentration.

Although samples of DMEAl showed elemental microanalyses (Al, C, H, N) that were in excellent agreement with a 1:1 adduct ratio, the ratio (amine:alane) from the NMR integration was consistently higher, at around 1.07. This probably reflects the inaccuracy inherent in the integration, particularly of such a broad signal.

Stability

In contrast to most of the trialkyls of group III, exposure of small quantities of DMEAl to the atmosphere did not result in spontaneous flaming unless the sample fell onto finely divided material. None was observed when DMEAl was repeatedly dropped onto filter paper or silica gel. However, ignition was observed after about 1 min when 6 cm³ was dropped onto a depth of 0.5 cm of vermiculite. Because the oxidation is exothermic, exposure of larger quantities to the air may result in spontaneous flaming even in the absence of finely divided material owing to self-heating.

The thermal stability of DMEAl was tested to ascertain whether its relatively low thermal stability represented a hazard, either to the producer, shipper or the user.

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Consequently, samples were heated in a differential scanning calorimeter (DSC) under a 6 mbar overpressure of argon; the heating rate was 5 °C/min. An endothermic event was detected in the temperature range 130–150 °C, presumably owing to rapid dissociation of the amine; the onset of an exotherm was detected at around 300 °C. This implies that if decomposition occurs below 200 °C, "runaway" via self-heating with its associated risk of explosion is not possible. The DSC of the solid adduct TMAAl was similar, endothermic events occurring at 63 and 109 °C, with an exotherm at 300 °C. The first endotherm occurs just below the melting point (actually 77–78 °C, which implies that a small amount of decomposition may have occurred during sampling), but thereafter, the thermal behavior is not significantly different from that of DMEAl.

A sample of DMEAl (15.5 g, 0.15 mol) was then held at 80 °C under 1.02 bar argon for 30 min in a high-pressure autoclave (HPA) of volume 0.08 dm³. Thereafter, at this initial temperature, an attempt was made to explode the sample using an electrically heated wire. The pressure rose to 16 bar over 25 min (corrected back to 80 °C) with a maximum rate of rise of 4 bar/min (in the interval 3–5 min): a very low value compared with materials conventionally described as explosive. Indeed, in an attempt to initiate a more violent response, the power in the heating wire was increased. However, this led to only a small increase in the rate of pressure increase, and in fact burnout of the heating wire soon resulted.

Samples of DMEAl held at 25 °C were found to give rise to gray deposits after about 1 week, even if held in the dark. The resulting supernatant still showed an adduct ratio of 1:1 on the rather inaccurate basis of integration of ¹H NMR signals. However, upon separation of the supernatant from the solid deposit, subsequent decomposition occurred more slowly: it was visible only after more than 3 weeks under the same conditions. The thermal decomposition of a freshly prepared sample appeared to be very dependent upon temperature: at 10 °C only minute traces of gray solid were visible after 6 weeks, even if exposed to daylight. Held at 5 °C, samples showed less than 5% decomposition (based upon precipitated Al) after 4 months. Similarly, a sample of the solid adduct, TMAAl, also showed considerable gray deposits after several months in a glass ampule.

DMEAl in a stainless steel bubbler was substantially depleted during MOVPE of Al_xGa_{1-x}As by evaporation at 40 °C under 0.25 bar,³⁴ and the remainder was held at ambient temperature for over 6 months. At the end of this time, much grey solid was present in the bubbler, as was observed *in vitro*, but there was also considerable buildup of gas pressure (presumably hydrogen). The clear, colorless liquid above the solid was found to consist of alane adduct in the ratio 1.47:1 amine:alane on the basis of elemental analyses. A liquid residue richer in amine than the starting material implies that much of the decomposition occurred during the period of nonuse at ambient temperature. Decomposition during evaporation in an open system at elevated temperature would be more likely to give a residue depleted in amine, as is shown in the next section. However, in a closed system, if a fraction of the sample decomposed to aluminum, hydrogen, and amine, then the last would combine with undecomposed DMEAl to give a higher overall amine:alane ratio, as observed.

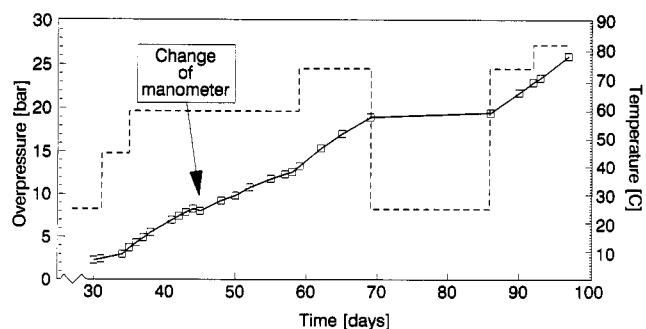


Figure 1. Cumulative buildup of overpressure (□) from DMEAl at various temperatures (---).

Because of the potential hazards associated with the pressure buildup, a sample of DMEAl (0.24 mol) was placed in a conventional stainless steel bubbler of 0.265 dm³ capacity, the outlet of which was fitted with a pressure gauge. The bubbler was held in a thermostatically controlled bath and the gradual increase in overpressure was monitored (above the 1 bar originally present). Because the NMe₂Et component of the adduct is a liquid of high vapor pressure, it will have a significant contribution to the total pressure in the bubbler only at low overpressures. In fact, it is a good approximation to assume that all pressure evolved is from hydrogen. Using this assumption, and further assuming that the AlH₃ moiety decomposes completely to the elements, then a total of 0.36 mol of hydrogen can be generated from this sample. At 25 °C, this is equivalent to a pressure of 34 bar in the vessel (based upon the van der Waals equation for hydrogen³⁷). The cumulative pressure as a function of time at various temperatures is shown in Figure 1 (all pressures are corrected back to 25 °C using the van der Waals equation). The experiment was terminated when the pressure reached 27 bar, although the pressure still appeared to be increasing linearly with time. From these data the following were concluded: the rate of increase in pressure is rather slow at room temperature, less than 0.1 bar/day; this rate rapidly rises with increasing temperature; the final pressure attained can be considerable; and there was no evidence that the pressure will asymptote to an equilibrium value below that for complete decomposition of the sample.

Upon attempting to open a sample of TMAAl held in glass, the top of the ampoule exploded and sent glass fragments around the glove box, showing that there was also considerable buildup of pressure (presumably also hydrogen) over this period. This highlights a potential hazard of handling alane adducts.

Because of the thermal instability of these compounds, the amount of usable precursor could be somewhat lower than the original sample. A more significant implication of this relates to the stability of dosimetry during deposition: if a sample begins as a 1:1 adduct but this ratio gradually rises, then the effective vapor pressure of the source will change with time. Nevertheless, although the shelf life of DMEAl is limited, the rate of change is unlikely to cause problems with variable dosimetry if it is stored at around its melting point (5 °C) and only held at room temperature during deposition.

Volatility and Vaporization Behavior

The vaporization behavior provides a further indication of the degree of stability at elevated temperatures. Using

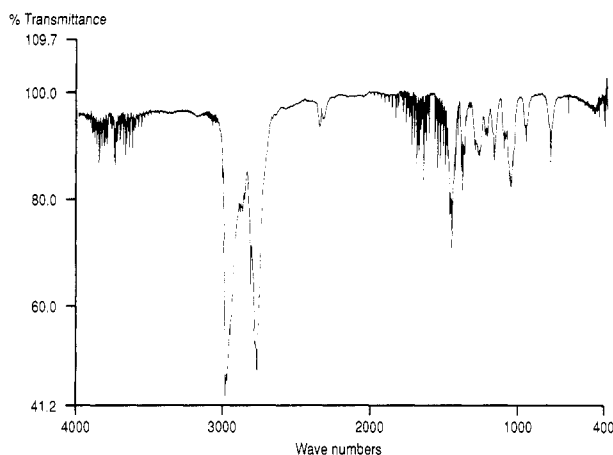


Figure 2. Gas-phase infrared spectrum of NMe_2Et (note bands of water vapor at 3756, 3652 and 1595 cm^{-1} and CO_2 at 2349 cm^{-1} due to incomplete purging of background gas in spectrophotometer.)

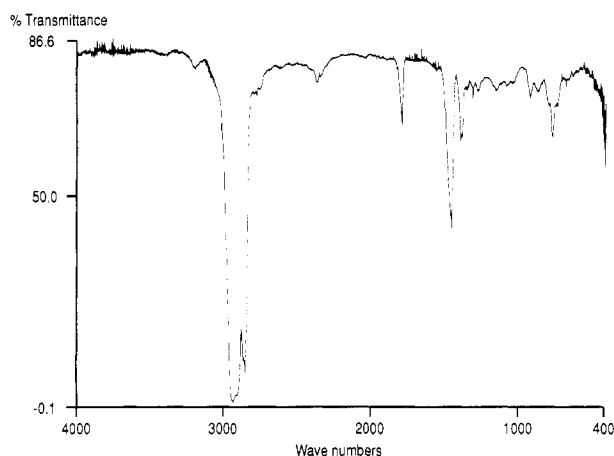


Figure 3. Gas-phase infrared spectrum of DMEAL.

a simple distillation bridge, DMEAL distilled at 50–55 °C/0.07 mbar into a receiver flask held at –78 °C. However, during distillation a white solid residue began to appear, usually about 20% of the original sample. This is almost certainly AlH_3 because, although itself involatile, upon addition of extra NMe_2Et , further adduct could be distilled. This indicates that the adduct is relatively weak because some incongruent vaporization of amine occurs under these conditions.

Because of this, the composition of the vapor over the compound at 25 °C was determined using infrared (IR) spectroscopy. Argon gas was bubbled through a sample of DMEAL and then passed through a gas cell. The entrained vapors were then analyzed using an FT-IR spectrophotometer and compared with a spectrum obtained from pure NMe_2Et . These spectra are shown in Figures 2 and 3. In addition to the bands around 2900–3000 cm^{-1} normally present in aliphatic organic compounds, the spectrum of pure NMe_2Et (Figure 2) shows intense bands around 2800 cm^{-1} characteristic of C–H vibrations α to the N of an amine. In contrast, the spectrum of DMEAL (Figure 3) shows only C–H stretching modes around 2900–3000 cm^{-1} . From this it can be concluded that at ambient temperatures DMEAL evaporates essentially as the intact adduct, even though it distills with substantial dissociation at higher temperatures in vacuo. Another characteristic feature of the IR spectrum is the pair of Al–H vibrations at 1790 and 1796 cm^{-1} .

The distillation conditions referred to above do not reflect accurately the vapor pressure of DMEAL because the quoted temperatures are those of the heating bath. More significantly, in such apparatus it was only possible to measure the pressure in the vacuum line, which was rather remote from the distillation flask. The determination of the true volatility of all alane adducts with amines is complicated by the aforementioned tendency to lose amine at elevated temperatures. This means that the vapor pressure as measured manometrically might be higher than the effective partial pressure of Al-containing species in the gas phase (that which determines the dosimetry of precursor in MOVPE or CBE). The manometric vapor pressure is the sum of the true vapor pressure of the DMEAL, the dissociation pressure of the amine from the adduct (the remanent AlH_3 being essentially involatile) and any hydrogen released upon decomposition.

The vapor pressure was determined manometrically and found to obey the following relationship in the temperature range $273 \leq T \leq 313$ K:

$$\log(P/\text{mbar}) = 10.85 + 3090/T \quad (1)$$

The values showed good sample-to-sample reproducibility, however, hysteresis observed upon cooling from the highest temperatures showed that irreversible decomposition occurred; presumably giving rise to hydrogen. Equation 1 implies a vapor pressure of 2 mbar at 20 °C, a value consistent with those from other authors.³⁶ The Trouton constant⁴³ implied by eq 1 is 150 J/(mol K), which indicates that dissociation occurs congruent with vaporization at elevated temperatures.⁴⁴

By comparing the growth rates of “ALAs” during MOVPE of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for DMEAL and the standard precursor Me_3Al , the vapor pressure of DMEAL was calculated to be 1.6 mbar at 40 °C:³⁴ approximately one-sixth of that predicted by eq 1. This assumes that the growth rates were limited by the rate of transport of the Al precursor,¹ which is very likely at the high growth temperatures used. The discrepancy in volatility probably arises mainly because prereaction during MOVPE removes substantial amounts of precursor from the gas phase.³⁴ A second effect is that the vapor pressure determined manometrically at 40 °C consists of the pressure of the DMEAL plus the dissociation pressure of free NMe_2Et , and probably one for hydrogen released upon partial decomposition.

Experimental Section

All manipulations were performed in vacuo or under an atmosphere of purified argon, using a vacuum line or a glovebox. Solvents were dried over molecular sieves and distilled in vacuo prior to use.

The ^1H NMR spectra were obtained in benzene- d_6 using a Bruker AC200 FT spectrometer; signals are quoted in ppm relative to Me_4Si . The gas-phase infrared spectra were obtained in a gas cell with quartz windows and path length of 10 cm using a Biorad FTS-45 infrared spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratories of Dornis & Kolbe, Germany.

Trace element analyses using inductively coupled plasma techniques were performed on the purified samples by the analytical department of Billiton Research B.V. The vapor pressure of DMEAL was measured manometrically by TNO, Zeijt, Netherlands.

(43) Glasstone, S. *Textbook of Physical Chemistry*, 2nd ed.; Van Nostrand: New York, 1946; p 457.

(44) Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Smith, L. M. *J. Cryst. Growth* 1988, 92, 37.

The following tests were performed to determine whether DMEAl is pyrophoric. Under an ambient atmosphere of 65% relative humidity, 0.5 cm³ of pure compound was syringed onto dried filter paper and observed for 5 min for signs of ignition or charring of the paper; this was repeated three times for a variety of mesh sizes of paper. Then under 70% relative humidity, 6 cm³ compound was added to a 0.5 cm depth of dried silica gel (6–20 mesh; around 35 g) or dried vermiculite (around 10 g), and observed for 5 min for signs of ignition.

To a stirred slurry of AlCl₃ (188 g, 1.41 mol) and LiAlH₄ (180 g, 4.74 mol) in pentane (720 cm³) was added NMe₂Et (410 g, 5.61 mol). The reaction was exothermic and so addition was continued to maintain steady reflux of the solvent (approximately 1.5 h). After complete addition, the liquid showed two phases. Stirring was continued overnight, after which the white precipitate was filtered off and the filtrate cooled to -25 °C. At around -15 °C white crystals began to separate from the filtrate. After holding at -25 °C overnight, the supernatant was decanted off. The sample was then recrystallized from fresh pentane (250 cm³) which was warmed to 35 °C and then cooled to -25 °C to yield white crystals of DMEAl, which melted at 5 °C. Yield: 465 g, 80% based upon AlCl₃. Freshly prepared DMEAl showed the following elemental analyses: C, 46.8; H, 13.6; N, 13.5; Al, 26.0%, whereas C₄H₁₄NAl requires C, 46.6; H, 13.7; N, 13.6; Al, 26.2%. After use in MOVPE at 40 °C followed by storage in the bubbler at ambient temperature for 6 months, the clear colorless liquid showed the following values: C, 51.4; H, 14.3; N, 14.9; Al, 19.3%. These values correspond to an average amine:alane ratio of 1.47:1.

Conclusions

An optimal synthesis of DMEAl, the 1:1 adduct of alane with NMe₂Et, is described; this could be applicable for the preparation of other alane adducts. Also reported are the properties of this compound, particularly those pertinent to its use for the deposition of Al-containing layers by MOCVD/MOVPE or CBE.

DMEAl is a volatile liquid at ambient temperatures which is rapidly decomposed upon exposure to the ambient

atmosphere. It slowly decomposes in a conventional, stainless-steel bubbler at room temperature, with the potential to generate high pressures of hydrogen eventually. It is not known whether this decomposition is self-limiting, so it is recommended that no more is placed in a vessel than can be withstood if the whole sample decomposes. Partially decomposed samples contain a higher amine:alane ratio than unity and are consequently less volatile. The rate of decomposition is very temperature dependent and is very low at or below the melting point. Therefore, it is recommended to store the precursor at this temperature or lower to avoid problems with loss of usable sample and long-term variability in dosimetry. Thermal instability is also a feature of the solid adduct TMAAl.

On the basis of DSC and HPA measurements, the thermal decomposition of DMEAl below 200 °C in the absence of oxygen should not represent an explosion hazard.

The distillation of DMEAl in vacuo is accompanied by some dissociation of the adduct, giving incongruent vaporization of amine and leaving an involatile residue of AlH₃; this shows that the adduct bond is relatively weak. In contrast, gas-phase infrared spectra show that DMEAl evaporates around ambient temperatures as the intact adduct. The volatility of DMEAl was determined by manometry in the temperature range 0–40 °C, and is convenient for use in MOCVD or CBE.

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