In-situ Fourier Transform Infrared Spectroscopy of Chemistry and Growth in Chemical Vapor Deposition

by

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Submitted to the Department of Chemical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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Abstract

Organometallic chemical vapor deposition (OMCVD) is a premier technique for synthesis of multilayer structures of III-V compound semiconductors (e.g. AlGaAs, InSb) used in electronic and optoelectronic applications such as diode lasers and detectors. The technique is attractive for large-scale manufacturing, but difficulties in run-to-run reproducibility and the lack in understanding of process chemistry limit the technology. This thesis summarizes new applications of Fourier transform infrared spectroscopy (FTIR) to address these problems.

A new fiber-optic-based (FOB) FTIR technique has been implemented as a remote in-situ monitor of organometallic concentrations in an OMCVD system. The measurement is based on molecular absorbance in the near mid-IR region (20,000-2400 cm⁻¹) by utilizing a seven-fluoride-fiber-bundle system and an InSb detector. Detection limits for various organometallic sources are investigated and determined to be acceptable for on-line concentration measurements in the delivery lines, as well as for detection of species in an OMCVD reactor under typical growth conditions. The performance of the set-up for measurement in the gas delivery system is demonstrated in monitoring of transients during turning on and off organometallic flow. The technique is sufficiently sensitive to detect the presence of volatile impurities, unsaturated delivery from solid organometallic precursors as well as condensation of precursor. Simple mathematical models are developed to identify problems of wall condensations. The set-up is used to gain insight into OMCVD growth using combinations of new organometallic sources. The FOB-FTIR technique is particularly useful for detecting parasitic Lewis acid-base reactions between group III and group V sources responsible for decreased OMCVD growth performance.

A new tool for investigations of organometallic decomposition reactions under OMCVD conditions was developed by coupling a pyrolysis gas cell and the FOB-FTIR operating at mid-IR region (3300-1100 cm⁻¹). The set-up is used
to investigate the decomposition chemistry of tris-dimethylamino-arsine [As(N(CH₃)₂)₃ or DMAAs], and the analogous phosphe(DMAP) and stibine (DMASb) compounds. These sources represent a new class of group V organometallic sources developed as a potential replacement for arsine and phosphine. Pyrolysis studies performed in hydrogen, deuterium and helium reveal that the compounds primarily decompose by homolysis of the E-N bond (E = P, As, Sb) leading to formation of dimethylaminyl radicals. The pyrolysis proceeds according to a first-order process, with activation energies of 50.6, 44.0 and 41.1 kcal/mol for DMAP, DMAAs and DMASb, respectively. The decomposition occurs at relatively lower temperatures than the trialkyl group V sources. Subsequent interactions of dimethylaminyl radicals result in the formation of methylmethyleneimine, dimethylamine, methyleneimine and methane. At temperatures higher than 550°C, the dimethylaminyl radicals decompose with generation of ammonia and methane as primary products. Since the decomposition of the dimethylaminyl radical could lead to incorporation of carbon and nitrogen impurities in the film, 550°C marks the upper limit of gas phase temperatures suitable for growth of high quality III-V compound semiconductors with these reagents.

The presence of a lone-pair orbital on the dimethylamino group raises the possibility of strong Lewis acid-base interactions leading to the formation of adducts with group III alkyls. *In-situ* FTIR and *ex-situ* nuclear magnetic resonance (NMR) techniques have been employed in investigations of gas phase interactions between tris-dimethylamino group V and trialkyl group III (R₃M; M = Al, Ga, In, R = alkyl) sources. Strong Lewis acid-base interactions are observed at room temperature and lead to formation of adducts. The group III atom coordinates with a nitrogen atom from DMAP to form low vapor pressure stable adducts. Adducts between group III and DMAAs decompose via exchange of alkyl and dimethylamino groups to form dimers of (MR₃N(CH₃)₂)₂ and As(N(CH₃)₂)(CH₃)₂. Exchange reactions also occur between DMASb and trialkyl group III leading to the formation of the group III dimers and SbR₃. The products of interactions adversely affect the OMCVD process. It is recommended that the use of tris-dimethylamino group V sources be restricted to low pressure OMCVD growth, and that the mixing time between the group III and V sources be reduced.

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To my dad and mom
This is for you
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Chapter 1:

OMCVD Technology and Chemistry

1.1 Introduction

Organometallic chemical vapor deposition (OMCVD) is a premier technology used for deposition of III-V compound semiconductors for electronic and optoelectronic applications\textsuperscript{1,2,3}. The OMCVD process, as shown in Figure 1, involves transfer of organometallic reagents in the vapor phase to a heated substrate where a thin solid film is formed through reactions of the organometallic reagents. The technique is attractive for large scale production, however the lack of on-line monitoring sensors and understanding of the process chemistry limit the technology.

Current OMCVD technology is typically carried out at reduced pressure near atmospheric conditions (1 < P < 760 torr) with limited monitoring of the organometallic concentration supplied to the reactor. Any fluctuation in the organometallic delivery, due to condensation, pre-reactions or varying generation of the organometallic vapor can only be detected in a post-morthern of the final layer structure. Most optoelectronic device applications involve quantum confinement effects which require the growth of multilayer structures, each layer consisting of high purity materials with exact composition, dopant concentration and thickness with accuracy down to 0.1 nm. The development of in-situ techniques for monitoring the growth process is therefore very important to ensure reproducible growth results.
Figure 1.1 Organometallic chemical vapor deposition (OMCVD) process and phenomena. (after reference 2)
The versatility of OMCVD stems from the availability of various organometallic sources. In the deposition process, these organometallic compounds remain intact or undergo gas phase and surface reactions depending on the growth conditions. The gas-phase reactions can be beneficial by increasing the reactivity of the species arriving at the substrate, or can be parasitic by leading to impurity formation and related changes in optical and electronic properties of the deposited layers. Understanding how the chemical structure of the starting organometallic sources affects the final properties of the epitaxial layers is therefore also critical to OMCVD. It is worthwhile as well to understand the possibility of interactions between organometallic sources at room temperature. If operating conditions are not right, gas-phase interaction between organometallic precursors might lead to reduced growth rates and enhanced impurity incorporation.

In this introductory chapter, applications of OMCVD of III-V compound semiconductors are discussed. The current state-of-the-art OMCVD systems are briefly reviewed. In-situ concentration monitoring techniques for OMCVD are surveyed along with Fourier Transform Infrared (FTIR) applications for OMCVD. A summary of group III and V organometallic sources used in OMCVD is given with discussion of Lewis acid-base interactions between group III and V organometallic precursors relevant to OMCVD. Finally the scope of the thesis is outlined.

1.2 OMCVD applications

Potential applications of III-V compound semiconductors in optoelectronic devices may be summarized in terms of the energy band gap
versus lattice parameter. In principle, it is possible to make light emitting devices or detectors covering the spectrum from far infrared (~ 12 μm) to near ultraviolet (~ 300 nm). Narrow band gap III-V materials, such as InAs, InSb, GaSb and AlSb, are useful for devices operating in the mid-infrared region from 2 - 5 μm range. Such devices would have applications in long wavelength fluoride optical fiber for communications, remote sensing and environmental applications.

Most of applications of OMCVD have been in the near IR region corresponding to the InGaAsP (λ ~ 1.3 - 1.5 μm.) and AlGaAs (λ ~ 0.8 μm.) materials. The InGaAsP system is used for diode lasers and detectors for fiber optic communications. InGaAs laser at 980 μm is used for pumping erbium doped optical fiber amplifiers. The AlGaAs system which takes advantage of lattice match with AlAs and GaAs is used commercially for making 0.8 μm laser in printers, compact disc players, as well as high power laser units for pumping of solid state lasers.

Visible diodes and lasers emitting in the red to yellow region have been developed based on the AlInGaP material system. These lasers have replaced the He-Ne lasers in bar code scanners and laser pointers. Recently, blue green emission has successfully been demonstrated in the InGaN system and blue diodes are commercially available. Addition of aluminum to the InGaN system will increase the band gap further, with promise the applications in the ultraviolet region.

Lattice parameters are included in the diagram, since lattice matching is important to the growth of multilayer structures. Large differences in lattice parameters cause dislocations which severely decrease device performance.
Figure 1.2  Lattice parameters versus band gap for compound semiconductors.  
(after reference 2)
1.3 OMCVD systems

An OMCVD system consists of three major parts: a gas handling system, a reactor and an exhaust system.¹ A typical set up of OMCVD is shown in Figure 3. The gas handling system functions as the source of organometallic vapor and hydrides, the place for metering the delivery of organometallic reagents and mixing the gas entering the reactor. The composition of the gas entering the reactor and the timing of delivery are crucial in determining the physical composition and structure of the film. The pyrophoric nature of the sources used in OMCVD requires the design of a vacuum-leak-tight gas handling system to prevent oxidation by oxygen and water vapor. The system is typically constructed of welded electropolished stainless steel tubing. In places where welding is not permissible, high-vacuum gas line fittings of metal to metal gaskets are used. Metal bellows seal valves with minimum dead volume are typically used. The system is equipped as well with a gas purifier to ensure a clean gas system down to 99.9999\% purity.

A liquid or solid organometallic reagent is typically transported in the vapor phase by flowing a known amount of carrier gas through the bubbler in which the organometallic source is kept. The amount of organometallic picked up is usually determined by the flow rate of the carrier gas, the source temperature and the total pressure of the bubbler. According to mass conservation and assuming saturation condition inside the bubbler, the relation between the flow rate of organometallic (Qₘ) and the carrier gas flow rate (Q₉) is represented by:
Figure 1.3  A schematic diagram of state-of-the-art OMCVD system consist of a gas handling, a reactor and an exhaust system.
\[ Q_s = Q_{CG} \frac{P_s}{P_r - P_s} \]  

(1.1)

where \( P_S \) and \( P_T \) are the source partial pressure and the total pressure of the bubbler, respectively.

The delivery of carrier gas to the reactor is metered by a mass flow controller. The pressure of the bubbler is typically regulated by a pressure controller system consisting of a capacitance manometer with feedback to a control valve. The bubbler is usually kept in a temperature controlled bath, which maintains the temperature within 0.1°C accuracy.

Typically the source bath temperature is kept at temperatures lower than room temperature to minimize source condensation in the delivery line and to circumvent the use of heated gas lines and valves. The pressure of the bubbler is also kept higher than the vapor pressure of the source to prevent accidentally boiling the source. The carrier gas flow to the bubbler is typically low, \textit{i.e.} \( \leq 500 \) sccm, to ensure complete saturation.

To ensure uninterrupted and stable delivery of organometallic precursors to the reactor, most gas handling systems are equipped with run-vent configurations. These configurations are crucial for growth of abrupt junction multilayer structures, such as devices containing multiple quantum-wells. At the earlier stage of "turn on" carrier gas flow to the bubbler, the organometallic flow experiences some transients. The run-vent set-up allows the flow of organometallic to be stabilized through the vent line before it is switched to the reactor (run line). This arrangement is essential for abrupt termination of the organometallic flow to the reactor. A constant flow of organometallic precursors in both the run and vent line is achieved by maintaining equal pressure of both lines. Pressure spikes can be avoided by maintaining a small pressure differential between the two lines.\textsuperscript{1}
There are more than five lines for organometallic precursors and hydrides in a typical growth reactor system. The organometallic flows are diluted with the carrier gas and premixed further before they are delivered to the entrance of the reactor. The gas flows over the substrate, which is typically held on top of a heated susceptor. Graphite or molybdenum are typical materials used. Heating is achieved resistively, radiatively or inductively. The temperature of the susceptor is typically measured by a thermocouple embedded in the susceptor. Thermal gradients above the substrate can create convection driven flows which superimposes on the main carrier gas flow to form complex flow fields. Conditions which lead to recirculation patterns have been explored through systematic fluid mechanic and thermal transport modeling of OMCVD reactors.9

For low-pressure reactor operation, a throttled or ballasted mechanical pump, capable of handling high gas loads is used. The reactor pressure is typically maintained by a throttle valve. The gas effluent containing unreacted organometallic reagents is treated in scrubbing units with activated charcoal or with a "burn-box" before being released to the atmosphere.

1.4 On-line monitoring of the OMCVD process

In most laboratories, OMCVD processes are operated in open loop configurations with no direct monitoring of the layer during the growth.1 The amount of precursor delivered to the reactor is generally unknown and is estimated based on the vapor pressure of the compound assuming saturation conditions in the bubbler. Any deviation from saturation that might occur at high flow rates cannot be detected. This problem is particularly acute for solid source precursors, such as trimethylindium (TMIn).10 The change in surface area during the evaporation leads to uncontrolled variations in the delivery rate,
and consequently, changes the In content in the deposited compound semiconductor. Deviations from the desired film properties are only detected in analysis of the final layered structure. Thus, a sensor system for monitoring organometallic delivery to the reactor is a key element for improving control in OMCVD.

Current sensor technology is based on the measurement of speed of sound of a binary gas mixture.\(^{10}\) According to the ideal gas law, the acoustic velocity \(c \text{ (m s}^{-1}\text{)},\) of a single species gas is related to the molecular weight by:

\[
c = \left(\frac{\gamma RT}{M}\right)^{1/2}
\]

where \(\gamma\) is the ratio of principal specific heats, \(C_p/C_v\); \(R\) is the universal gas constant; \(T\) is the absolute temperature and \(M\) is the molecular weight of the gas species. For a binary gas mixture, assuming an ideal mixture, equation (1.2) is applicable by replacing \(\gamma\) with \(\gamma^*\) and \(M\) with \(M^*\), with:

\[
\gamma^* = 1 + \left[\frac{x}{(\gamma_2 - 1)} + \frac{(1-x)}{(\gamma_1 - 1)}\right]^{-1}
\]

\[
M^* = (1-x)M_1 + xM_2
\]

where \(M^*\) is the mean molecular weight of the binary mixture and; \(M_i\) is the molecular weight of the species \(i\), \(\gamma_i\) is the specific heat ratios of species \(i\), and \(x\) is the mole fraction of species 2.

The acoustic measurement is implemented by time-of-flight technique. This is done by timing the transit of an acoustic pulse between two ultrasonic transducers held at a known separation in the gas mixture. The transit time, \(\tau\) is related to the acoustic velocity \(c\) by:

\[
\tau = \left(\frac{l}{c}\right) + \Delta \tau
\]

where \(l\) is the distance of the transducers and \(\Delta \tau\) is a constant delay time. This
set-up, which is known commercially as the "Epison", is typically installed in between the bubbler and the pressure controller and typically kept at the pressure similar to the bubbler pressure.\textsuperscript{11} This technique has been used in controlling the delivery of TMIn in OMCVD, but the system is restricted to pressure above 400 torr and is not chemically specific.

Development of alternative \textit{in-situ} monitoring techniques is crucial to the OMCVD process. Monitoring of low vapor pressure organometallic sources which are designed to reduce carbon incorporation is of particular interest. Some of these alternative organometallic sources have low vapor pressures and to increase the delivery, the bubbler temperature is typically higher than room temperature. The pressure inside the bubbler is often kept at lower than 400 torr to increase the delivery, making it difficult, if at all possible to use an ultrasonic measurement. These conditions potentially can lead to condensation which would affect the supply of organometallic reagents to the reactor.

The relative high pressure reactive OMCVD environment necessitates the development of optical techniques. Hebner \textit{et al.}\textsuperscript{12} demonstrated the use of ultraviolet absorption spectroscopy technique for measuring the absolute concentration of organometallic reagents inside an OMCVD reactor and the transient switching response. The advantage of the UV technique is the large absorption cross section of organometallic sources in this frequency region which makes it possible to measure the organometallic and hydride pressure using relatively short optical pathlengths. The utility of this technique for online monitoring of concentrations of organometallic compounds is, however, restricted by photo-stimulated decomposition of the compounds.

Infrared spectroscopy is potentially useful for monitoring the OMCVD process, since it directly probes chemical bonds, is sufficiently simple for manufacturing applications and does not cause premature decomposition of the
organometallic reagents. The application of infrared spectroscopy for in-situ concentration monitoring is discussed in the next sections.

1.5 Applications of Fourier Transform Infrared Spectroscopy in OMCVD

1.5.1 Applications for in-situ concentration monitoring

In infrared spectroscopy, transmission of IR light through the sample is monitored as a function of wavelength. Molecules are identified on the basis of characteristic frequencies corresponding to vibrational excitation of the molecule. The absorbance of a molecule is related to the concentration according to Beer's law:

\[ A = \log \frac{I}{I_0} = -\alpha l c \]  

(1.6)

where \( A \) is the absorbance at a given wavelength, \( I/I_0 \) is the ratio of absorbance intensity between the sample (I) and the background (I0), \( \alpha \) is the absorptivity or the absorbance cross section of the molecule, \( l \) is the sample path length and \( c \) is the concentration of the organometallic precursor.

The use of IR techniques for OMCVD offers wide range of advantages. Most organometallic molecules have absorbance bands in the infrared and the technique is non-intrusive. Unlike the UV technique, the low energy of the infrared light does not promote photochemical reactions of the organometallic source.

Breiland and Ho review examples of infrared spectroscopy applications for monitoring concentrations of chemical species in CVD growth systems. Suzuki et al. monitored the concentration of SiCl3H in real time control of liquid flow from a vaporizer. Shibata and Sugawara used the infrared
technique to monitor the consumption of SiH₄ from effluent of a CVD reactor. Recently, O'Neil et al. ¹⁷ demonstrated the use of FTIR spectroscopy in CVD systems for real time monitoring of the concentration of tetraoxysilicate and ozone which are introduced into a SiO₂ CVD reactor and the trimethylphosphine concentration used for doping Silicon CVD process.

The application of FTIR spectroscopy in OMCVD has been limited, especially in manufacturing environments, due to difficulties in maintaining a long purged optical path for guiding the IR signal between the spectrometer system and a gas sensor for each organometallic line. However, recent development in IR fiber technology, especially in chalcogenide and fluoride fibers, makes it possible to extend the FTIR technique beyond bench top applications to in-situ remote sensing applications. ¹⁸ Fluoride fibers are suitable for monitoring systems with vibrational absorption bands in the range of 20,000-2000 cm⁻¹. With a 90% signal transmission over 5 meters, the fluoride fibers are suitable for remote sensing applications as previously demonstrated in in-situ analysis of plastic film manufacturing. ¹⁸ The chalcogenide fibers transmit light in the 3300-900 cm⁻¹ range, which is the primary region of interest of studying organometallic chemistry, with limited transmission in 2300-1900 cm⁻¹. Remote sensing applications using this fiber are limited by absorption, which results in a 38% loss signal over a one meter fiber length. Figure 1.4 shows the operating windows of these two fibers along with other optical materials and IR detectors which are used in this thesis. Applications of the fluoride fibers to in-situ concentration monitoring of organometallic delivery is described in Chapter 2 of this thesis. Chapter 3 explores the use of chalcogenide-fiber-based FTIR for gas-phase decomposition studies of new organometallic sources, tris-dimethylamino group V compounds. Previous FTIR investigations of OMCVD gas phase chemistry are discussed in the next section.
Figure 1.4  Transmission range of detectors, fibers and optical windows used in this thesis.
1.5.2 Applications for understanding reaction mechanisms

Infrared spectroscopy has primarily been used to gain insight to the chemical mechanisms underlying OMCVD as discussed in the review by Breiland and Ho. In this section, the discussion will be limited to applications of FTIR and dispersive IR technique. Most of the studies were performed using ex-situ techniques, which relied on sampling gases from hot reaction zones. Nishizawa and Nihira implemented such an ex-situ FTIR technique in the studies of the mechanism of silicon deposition from SiCl₄, SiCl₃H, SiCl₂H₂ and SiH₄/HCl gas mixtures. Nishizawa and Kurabayashi studied the deposition of GaAs from TMG and arsine and showed that decomposition of the reactants produce methane gas which had clear identifiable spectra features compared to the undecomposed TMG and arsine. Nishizawa et al. also used the IR spectroscopy to observe chemical species evolving from the growth of GaAs using AsCl₃ and Ga, as well as the GaCl₃/AsH₃ system. Denbaars et al. used the ex-situ FTIR spectroscopy for monitoring TMG decomposition from an OMCVD growth reactor. Fan et al. studied the decomposition of tertiarybutylphosphine by sampling the exhaust gas stream of an OMCVD reactor. Although the application of ex-situ techniques for sampling gas from the reactor has the advantage of simplicity and can provide quantitative measurements of species concentrations, the major drawback is the requirement of sampling probes which restrict the possibility of monitoring reactive species.

In-situ FTIR techniques, on the other hand, allow direct monitoring the absorption spectrum of hot, reacting gas in a CVD reactor. Armstrong et al. used the in-situ technique to monitor arsine and trimethylgallium reactions from
a horizontal OMCVD reactor. However, this in-situ approach for monitoring a CVD reactor directly is limited due to poor spatial resolution of the FTIR technique. The absorbance measurement is averaged over total infrared pathlength, and the size of the infrared beam is large for a conventional incoherent source (about 10 mm). This features make quantitative measurement difficult, especially since spatial variations in concentration and temperature occur over a few mm in typical CVD reactors.

In this thesis, in-situ FTIR cf reactive mixtures in a pyrolysis gas cell is used in mechanistic studies of the decomposition of new organometallic sources: tris-dimethylamino group V compounds. This pyrolysis gas cell minimizes temperature and concentration gradients across the sampling region without losing the capability of monitoring reactive species. Furthermore, the approach allows study of kinetics under flow conditions similar to those found in OMCVD systems. Chapter 3 presents an investigation of decomposition chemistry of tris-dimethylamino compounds.

1.6 Organometallic reagents

Trimethyl group III sources (M(CH3)3, M = Al, Ga and In) and group V hydrides (AsH3 and PH3) are traditionally used as sources in OMCVD. Epitaxial films of GaAs and InP have been grown successfully using these compounds with low levels of carbon incorporation. In some cases, however, such as in the growth of AlGaAs, the use of these conventional sources leads to high levels of carbon incorporation. Increasing safety concern over the use of toxic hydride gases has pushed the search for alternative organometallic sources. Mechanistic studies of reactions of organometallic sources have provided useful insight into better design and use of new reagents, as nicely described in a recent review.
article by Jones.\textsuperscript{25} The following description highlights important results relevant to this thesis.

1.6.1 Alternative group III sources

Comparison of GaAs growth using arsine and two different gallium sources trimethylgallium (Ga(CH\textsubscript{3})\textsubscript{3} or TMG) and triethylgallium (Ga(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} or TEG) illustrates the role of chemistry in carbon incorporation.\textsuperscript{2} The growth using TMG tends to incorporate more carbon into the film compared to TEG. The carbon atom which occupies the group V site is a p-type impurity. To decrease the amount of carbon incorporation to an acceptable level (\(\leq 10^{14}\) atom/cm\textsuperscript{3}), the growth needs to be performed at high arsine to TMG ratios. The mechanism of carbon incorporation has been studied experimentally and in simulations.\textsuperscript{2} The mechanism of carbon incorporation, is believed to occur through surface reactions of GaCH\textsubscript{3}. Hydrogen abstraction from the methyl leads to the formation of the highly reactive gallium methylene (GaCH\textsubscript{2}). Subsequent reactions of the methylene with an exposed Ga atom leads to the incorporation of carbon on the arsenic site.\textsuperscript{26}

In the presence of absorbed As-H the highly reactive methylene may be hydrogenated back to GaCH\textsubscript{3}, which can desorb the methyl radical leading to the formation of a GaAs film. Thus, an increase in hydrogen on the surface through the introduction of additional arsine leads to reduced carbon incorporation. This hypothesis is consistent with growth observations showing that large V-III ratios are necessary to reduce the amount of carbon incorporation.

In growth with TEG, the level of carbon incorporation is reduced significantly and a high ratio of arsine to group III species is no longer
necessary. Mechanistic studies of the decomposition of TEG reveal two channels of decomposition, the first is homolysis of the Ga-C bonds leading to the formation of ethyl radicals, and the second is through β-hydride elimination producing ethylene (C₂H₄). The availability of the second channel provides an alternative pathway for hydrocarbon desorption from the growth surface.

Replacing the methyl group by the ethyl group seems to be a simple solution to alleviate carbon incorporation from any of the group III sources. In the growth of AlGaAs film, more severe problems of carbon incorporation are observed in the growth using trimethylaluminium (Al(CH₃)₃ or TMA). The stronger bond of the Al-CH₃ (65 kcal/mol) compared to Ga-CH₃ (59 kcal/mol) bonds presumably the reason behind this difference. Similar to the gallium case, the AlGaAs growth using triethylaluminium (Al(C₂H₅)₃ or TEAl) and TEG results in significant reductions in the level of carbon. However, the vapor pressure of TEAl (0.04 torr @ 27°C) is too low to be useful for manufacturing processes.

Significant effort has been placed on finding alternative aluminum sources which lead to low carbon incorporation and have a significant vapor pressure. Some of the most successful efforts have been sought through the utilization of Lewis acid-base interactions between aluminum hydrides and amines. Examples of these sources include trimethylamine alane AlH₃(N(CH₃)₃), the bis adduct of trimethylamine alane (AlH₃(N(CH₃)₃)₂) and ethyldimethylamine alane (AlH₃(N(C₂H₅)(CH₃)₂)). The design of these compounds is very suitable for low carbon incorporation, since they do not contained any Al-C bond and have acceptable vapor pressures to be used for OMCVD (2 torr @ 25°C). The compounds decompose at relatively low temperatures by breaking the weak Lewis acid-base interaction. The resulting AlH₃ is very unstable and reacts readily to form aluminum.
The use of the alane compound along with TEG and arsine\textsuperscript{32} in low pressure growth has resulted in low carbon containing AlGaAs. On the other hand, the use of TMG as the gallium source with the alane and arsine at low growth pressure (<150 torr) resulted in carbon incorporation.\textsuperscript{32} Atmospheric pressure growth of AlGaAs film using AlH\textsubscript{3}(N(CH\textsubscript{3})\textsubscript{3}), TMG and arsine resulted in premature reactions leading to the darkening of the reactor inlet.\textsuperscript{31,33} Infrared experiments indicated that transalkylation occurred between TMG and the alane source\textsuperscript{25} resulting in the formation of Al-Me and Ga-H compounds in the gas phase. The formation of Al-Me led to carbon incorporation into the film.

Other routes for finding alternative aluminum sources have been through the use of more bulky trialkylaluminum sources. The design of these sterically hindered molecules is to avoid formation of dimer molecules, which are observed for TMAI and TEAl. These bulky aluminum sources are expected to have higher vapor pressure compared to TEAl and at the same time decrease the bond energy of aluminum to carbon resulting in lower decomposition temperature. Triisobutylaluminum ((C\textsubscript{4}H\textsubscript{9})\textsubscript{3}Al or TIBAl) and tritietyributylaluminum ((C\textsubscript{4}H\textsubscript{9})\textsubscript{3}Al or TTBAI) are examples of such sources.

TIBAl has been used in the AlGaAs growth using organometallic molecular beam epitaxy (OMMBE)\textsuperscript{34}, which is an alternative growth technique operated under high vacuum conditions. The OMMBE growth using TIBAl, TEG and arsine\textsuperscript{34} showed a three order of magnitude reduction in carbon incorporation at low temperature compared to TEAl. This behaviour was attributed to the lower activation energy of olefin elimination of TIBAl (26.6 kcal/mol) compared to TEAl (30.1 kcal/mole).\textsuperscript{25} The use of this compound for higher substrate temperatures (>560°C), however, led to increase in carbon incorporation. Surface chemistry studies of Al deposition suggested that at high temperature β-methyl elimination pathways became kinetically competitive.
leading to the formation of Al-CH\(_3\) species.\(^{35}\) These growth characteristics prevented the use of this source in high temperature OMCVD growth of AlGaAs.

The use of TTBAI is currently being explored for OMCVD applications. The compound seems to be promising since the activation energy of olefin elimination of this compound is expected to be similar to TIBAI and the possibility of forming Al-CH\(_3\) species is not likely. The use of TTBAI for aluminum CVD showed significant reduction in the amount of carbon incorporation\(^{36}\) compared to the growth using TIBAI and suggest this sources as a potential candidate for OMCVD growth of Al-containing III-V materials. The gas-phase decomposition pathways of this molecule are explored in Appendix A, and examples of TTBAI delivery and possible interactions are discussed in Chapter 2.

Both TIBAI and the alane compounds are known to slowly decompose even at room temperature. TIBAI tends to decompose to give a volatile species diisobutylaluminium hydride.\(^{25}\) The trimethylaminealane is also observed to decompose to form a volatile aluminum compound and hydrogen. These premature reactions in the bubbler may effect the delivery of this compound for the use in production. The development of in-situ monitoring for measuring precursor delivery is therefore needed and it will be discussed in Chapter 2.

Severe delivery problems have been reported for the use of trimethylindium (In(CH\(_3\))\(_3\) or TMIn) for indium based materials.\(^{25}\) TMIn is a solid source and difficulties arise due to the continual change in surface area of the evaporating solid resulting in fluctuation in the delivery rate.\(^{10}\) Efforts at improving the stability of delivery using alternative liquid In sources have had limited success. The use of triethylindium (In(C\(_2\)H\(_5\))\(_3\) or TEIn) results in parasitic room temperature pre-reactions with PH\(_3\).\(^{37,38}\) Ethylidimethylindium,
which is a liquid, has been tried for growth of InP. Although the compound has reasonable vapor pressure (0.85 torr at 17°C)\textsuperscript{39}, it is observed to decompose in the bubbler to produce TMIn and TEIn.\textsuperscript{40} Constant delivery of indium to the reactor is then difficult to achieved, because of the difference in vapor pressure of TMIn and TEIn. The focus has therefore been on the development of concentration monitoring and control scheme for TMIn.\textsuperscript{25}

1.6.2 Alternative group V sources

Group V organometallic reagents are needed for replacing the use of toxic hydride gases arsine and phosphine. These alternative sources should be liquids with reasonable high vapor pressure, be stable for long term storage, but also decompose at lower temperatures than the hydride gas sources. They should furthermore not produce any impurities adversely affecting device performance.

The use of trialkylarsenic (As(CH\textsubscript{3})\textsubscript{3} and As(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}) as alternative sources in combination with trimethylgallium to grow GaAs by OMCVD results in high carbon incorporation.\textsuperscript{41,42} The absence of arsenic hydrogen species is believed to make it difficult for the alkyl group to leave the surface leading to the incorporation carbon to the film. A GaAs growth study using TMG and \textsuperscript{13}C labeled trimethylarsenic (TMAs or As(CH\textsubscript{3})\textsubscript{3}) shows that some of the carbon from the arsenic source is incorporated to the film.\textsuperscript{43} In fact, trimethylarsenic has been effectively used as the source of carbon doping for GaAs growth.\textsuperscript{44}

More successful results have been achieved using alkyl hydride arsenic sources, which have one or more As-H and As-C bonds. Among the alkyl hydride sources used in OMCVD, the most successful is tertiarybutylarsine ((C\textsubscript{4}H\textsubscript{9})AsH\textsubscript{2} or TBAs). TBAs is a liquid source with a high vapor pressure of 81 torr @ 20°C. The use of TBAs with TMG has allowed growth of n-type GaAs
with low impurities level compatible to those grown with arsine. The combination of TBAs and TEG produces n-type films with carbon levels below the detection limit. Pyrolysis studies showed that TBAs decomposed at 425°C (50% decomposition). This temperature was much lower than that observed for arsine, which pyrolized at 575°C.

Alternatives to PH₃, have been pursued with similar approaches to those for arsenic sources. Trialkyl phosphorous sources (trimethyl and triethylphosphorous) are too stable to be used for typical growth conditions, in fact they form adducts with trimethylindium which do not contribute to growth of InP films. The alkyl hydride sources are again found to be more promising. The use of tertiarybutyl phosphine (TBP or P(C₄H₉)₂H) and TMIn produced InP films with excellent film quality compatible to those observed PH₃. The vapor pressure of TBP is relatively high (114 torr at 10°C) and is suitable for manufacturing purposes. The compound decomposes at significantly lower temperature (450°C for 50% decomposition) compared to the decomposition temperature of phosphine.

Stibine, SbH₃ cannot be used for growth of Sb based compound semiconductors due to the low thermal stability of the source. Trimethylantimony (TMSb or Sb(CH₃)₃) has been used for growth of relatively high quality InSb in combination with TMG and TMIn, respectively. However, TMSb decomposes at a relatively high temperature compare to the melting point of InSb at 525°C. The use of TMSb in the growth of GaSb and AlGaSb could potentially lead to the increase in the amount of carbon incorporation in the film, analogous to observation in the growth of As based film using trimethyl sources. There is a need for alternative sources which pyrolize at lower temperature than TMSb and at the same time lead to reduced amounts of carbon incorporation.
The low thermal stability of Sb-H containing molecules limited the design of an alkyl hydride source analogous to the arsenic and phosphorous precursors. Hendershot and Berry, have successfully synthesized several relatively stable alkylhydride stibine, including neopentylstibine ((Me\(_3\)CCH\(_2\))SbH\(_2\)) and trimethylsilylmethylstibine ((Me\(_3\)SiCH\(_2\))SbH\(_2\)), as possible precursors for OMCVD. However, up to this date, the use of these compounds for epitaxial growth of antimony based film has not yet been reported.

Sterically hindered or bulky ligands of trialkyl sources have been considered as an alternative strategy. Triethylantimony (Et\(_3\)Sb) has been used along with trimethylindium in the growth of InSb at temperature as low as 410°C. Carbon incorporation in the film is found to be lower compared to those observed using TMSb. The use of triisopropylantimony (Sb(C\(_3\)H\(_7\))\(_3\)) has been explored, and resulted in lower InSb growth temperature to 350°C. However, the low vapor pressure of this source (0.4 torr at 25°C) resulted in a low growth rate < 0.4 \(\mu\)m/h.

Efforts to improve the growth rate by increasing the vapor pressure of the organometallic source while maintaining low decomposition temperature have been made by using mixed alkyl sources, specifically, tertiarybutyldimethylantimony (Sb(C\(_4\)H\(_9\))(CH\(_3\))\(_2\) or t-BuSbMe\(_2\)). OMCVD growth using t-BuSbMe\(_2\) and TMIn at 475°C resulted in films with higher mobility compared to those grown used TMSb. t-BuSbMe\(_2\) decomposes at relatively lower temperature (50% decomposition at 400°C) compared to TMSb thus permitting the growth at lower V/III. However, at temperature lower than 425°C the growth rate of InSb is < 0.2 \(\mu\)m/h. Alternative antimony precursors need to be developed to improve the growth process.
1.7 New alternative sources tris-dimethylamino group V compounds

*Tris*-dimethylaminoarsine (DMAAs), *tris*-dimethylaminophosphine (DMAP) and *tris*-dimethylaminostibine (DMASb) represent a new family of reagents for growth of III-V compound semiconductors.\(^{56}\) These reagents are distinct from previously studied organometallic compounds by their lack of direct group V - carbon or hydrogen bonds, and the presence of group V - nitrogen bonds. The molecules have been designed to circumvent problems of carbon incorporation often encountered in growth with trialkyl sources. They are also expected to have a relatively low decomposition temperature because of the weaker strength of the group V atom bond to nitrogen, as compared to the bond to carbon.\(^{57}\) The *tris*-dimethylamino reagents also represent the least bulky nitrogen, containing organometallic sources stable enough and with sufficiently high vapor pressures to be used in OMCVD.\(^{58}\)

Organometallic molecular beam epitaxy (OMMBE) studies by Abernathy *et al.*\(^{59}\) have demonstrated that GaAs films, with no detectable carbon, may be grown at relatively low temperatures (~450°C) without precracking when using trimethylgallium (TMG) and DMAAs. Salim *et al.*\(^{60}\) used mass spectroscopy to investigate reactions of DMAAs on GaAs surfaces under OMMBE conditions. DMAAs was observed to completely decompose at temperatures as low as 450°C. Two major decomposition pathways were proposed, the first involving a simple scission of the arsenic-nitrogen bond, the second entailing a β–hydrogen elimination reaction to form either aziridine or methylmethyleneimine and absorbed surface hydrogen as shown in Figure 1.5. The presence of hydrogen on the surface was believed to be important in reducing carbon incorporation during growth with TMG. These decomposition pathways have recently been
confirmed by Xi et al. in temperature programmed desorption (TPD) investigations.\textsuperscript{61}

OMCVD of GaAs with TMG and DMAAs in the temperature range of 550-700°C has been reported by Zimmer et al.\textsuperscript{62} No nitrogen incorporation was detected in GaAs grown at 650°C, while AlGaAs grown at 700°C appeared to be contaminated by nitrogen.\textsuperscript{5} InP films grown by using trimethylindium (TMIn) and DMAP were specular, with no detectable nitrogen or carbon incorporation.\textsuperscript{57} The growth of InSb with TMIn and DMASb, without significant impurity incorporation, has been reported.\textsuperscript{63, 64}

It was thought that the dimethylamine group would react with methyl from group III source to form stable compound trimethylamine.\textsuperscript{5} This compound has been used in design of the adduct Al precursors, (e.g. trimethylamine alane) and is known to be stable and not to interfere with the film during the growth.\textsuperscript{25} However, the presence of the dimethylamine ligands are likely to increase the chance of prereactions between with the group III sources through Lewis acid-base reactions.

\section*{1.8 Interactions between group V and group III sources in CMCVD}

Room temperature Lewis acid-base interactions between group V and group III sources are possible in many OMCVD growth systems. The interactions involve sharing of a lone pair electrons donated from group V atom (Lewis base) with group III atom which has one empty orbital to fill. The reaction can be summarized as follow:

\[ MR_3 + ER_3 \leftrightarrow R_3M:ER_3 \] (1.7)
Figure 1.5  Surface decomposition mechanisms of tris-dimethylamino arsine.

(after reference 60)
where M is group III atom, E is group V source and R is alkyl or hydrogen molecules. The product of the interaction is referred to as an "adduct". Liquid phase investigations have established the equilibrium relation between reactants and adducts. For many common organometallic precursors, the adduct bond is relatively weak and the rate of dissociation of the adduct is typically \( \leq 25 \) Kcal/mole.65

In OMCVD, gas phase Lewis acid-base interactions between group III and V sources are likely to occur as the organometallic sources are mixed upstream of the reactor entrance. The equilibrium reaction between the reactants and the adduct is similar to those observed in the liquid phase (e.g., 1.7). However, it is also possible that some adducts have a lower vapor pressure than the constituents, therefore could condense on the reactor wall. The condensation process drives the reactions toward the formation of more adduct and results in consumption of precursors, which results in a reduced growth rate.

Subsequent interactions of the condensed phase may lead to the formation of polymeric or volatile by-products which are transported to the growth region along with unreacted organometallic precursors. The formation of low vapor pressure adducts have been reported in the interactions of trimethylgallium and ammonia in the growth of GaN 66 as well as in the InP growth using phosphine and trimethylindium or triethylindium.67 In the trimethylgallium and ammonia mixture, the ligand elimination reactions is believed to occur according to:

\[
n(CH_3)_3Ga:NH_3 \rightarrow ((CH_3)_2Ga-NH_2)_n + nCH_4 \quad (1.8),
\]

where methane gas is the volatile by-products and the formation of \(((CH_3)_2Ga-NH_2)_n\) leads to a black deposit near the entrance of the reactor.

The relative strengths of the Lewis acids and bases play an important role in the possibility of the formation of the adducts. For group III sources, the
strength of acidity is strongest in Al, and weakest for In. For group V atoms, the base strength ranks as follow: N > P > As > Sb. Steric and electronic effects also contribute to the sequence of the base strength toward a group III acceptor. For example, for trimethylgallium: Me₂NH > Me₃N > NH₃ > MeNH₂.⁶⁵

Little has been reported on Lewis acid-base reactions between new alternative organometallic sources. This thesis addresses two cases of detrimental growth effects related to Lewis acid-base reactions. Chapter 4 explores acid-base reactions of tris-dimethylamino group V sources with trialkyl group III sources. Tris-dimethylamino group V sources are distinct from other sources used in OMCVD since each contains 4 potential base sites; one on the group V metal and the other three on dimethylamine groups. The study is carried out using in-situ FTIR spectroscopy, which is very suitable for understanding complex interactions of the acid-base reactions relevant to OMCVD.⁶⁸

1.9 Scope of this thesis

This thesis consists of two major portions: the first is investigation of in-situ FTIR applications for understanding chemistry and on-line concentration monitoring in an OMCVD growth system, and the second is gas-phase decomposition chemistry and interactions of new tris-dimethylamino group V compounds.

Chapter 2 demonstrates applications of fiber-optics based FTIR for in-situ remote on-line monitoring of organometallic concentration both in OMCVD delivery lines and from a reactor. The set-up which is based on fluoride optical fibers is used to measure concentration in terms of the absorbance of organometallic compounds in the alkyl (C-H) stretching region at 2700-3200
cm$^{-1}$. Calibration plots of absorbance versus concentration are made for various organometallic sources including trimethylgallium (TMG), triethylgallium (TEG), trimethylindium (TMI), tris-dimethylaminophosphorous (DMAP), tertiarybutyl phosphine(TBP) and trimethylantimony (TMSb). Different optical fiber systems and IR detectors are evaluated. Optimized performance is achieved by using an InSb detector and a seven-fluoride-fiber-bundle system. With a 10 cm sampling cell and one second scan, the minimum detection limit is determined to be 0.05 torr for trimethylgallium and trimethylindium at room temperature. This limit is acceptable for manufacturing application. The sensitivity of the technique increases with more C-H bonds; for example in DMAP with 18 C-H bonds the detection limit is determined to be 0.006 torr.

The technique is demonstrated for monitoring the transient behavior of source delivery during initial flow of carrier gas to the bubbler. Examples of transient deliveries from a bubbler that is maintained at lower than room temperature show no sign of condensation. Delivery from a bubbler which is maintained above room temperature shows a strong dependence on the gas line temperature. A simple mathematical model of the transient behavior is developed and used to identify the problem of condensation in the delivery line.

The performance of the technique is compared to measurements based on the ultrasonic principle in the delivery of the new organometallic source tritiarybutylaluminum (TTBAI). The ultrasonic measurement shows an ever decreasing concentration whereas the FTIR monitoring shows that TTBAI is delivered together with isobutene and isobutane, decomposition products of TTBAI in the bubbler. The chemical selectivity of the FTIR technique is determined to be important for providing more accurate measurement OMCVD feed concentrations.

Lower noise levels can be achieved by using longer scan time, and thus
allows *in-situ* monitoring of organometallics and hydride gases in an OMCVD reactor. *In-situ* concentration monitoring in an OMCVD reactor is successfully implemented in conditions similar to those used in successful growth of epitaxial films. The FTIR set-up is effective in monitoring delivery problems from chemical interactions and fluctuations in vapor pick up from TMIn. The FOB-FTIR is also used to gain insight into AlSb OMCVD growth using combination of new sources, particularly for detecting parasitic Lewis acid-base reactions responsible for decreased OMCVD performance.

Chapter 3 describes the applications of chalcogenide fiber-optic-based *in-situ* FTIR spectroscopy for understanding decomposition mechanisms of trisdimethylamino-phosphine, -arsine and -stibine. The studies were carried out in a pyrolysis gas cell which allowed *in-situ* monitoring and direct analysis of decomposition products based on a simple reactor model. The design of the cell is discussed in detail, and the performance of the set-up is demonstrated with decomposition of trimethylgallium and trimethylindium as test cases. The results show good agreement with literature data.

The primary decomposition pathway for tris-dimethylamino compounds is homolysis of the E-N (E = P, As, Sb) bond, leading to the formation of dimethylamininyl radicals. Subsequent interactions of dimethylamininyl radicals result in the formation of the stable products: methylmethylenimine, dimethyldimine, methylenimine and methane. The pyrolysis proceeds according to a first-order process, with activation energies of 52.6, 44.0 and 40.9 kcal/mole for DMAP, DMAAs and DMASb, respectively. At temperatures higher than 550°C, the dimethylamininyl radical decomposes, with the generation of ammonia and methane as primary products. The effect of surface reaction on the degree of decomposition is analyzed as well by packing part of the gas cell by large surface area of SiO2 and GaAs. The decomposition is observed to be
surface selective. In the presence of a large surface area of GaAs, the decomposition temperature is lowered by 100°C for tris-dimethylamino-arsine, however the effect is not observed much in the present of high surface area of SiO₂. Molecular beam mass spectrometry technique verifies the FTIR results and provides complementary information which is not observed by the infrared technique.

The in-situ FTIR technique is also utilized in studies of the decomposition of tritertiarybutylaluminum(TTBAI). In hydrogen, TTBAI decomposition is observed to proceed by homolysis of Al-C bond to yield tertiarybutyl radicals. Subsequent reactions of the tertiarybutyl radicals lead to the formation of equal amount isobutane and isobutene. The pyrolysis reaction has an apparent first order behavior with an activation energy of 32.3 kcal/mole.

Chapter 4 describes in-situ FTIR spectroscopy and ex-situ NMR investigations of acid-base interactions in mixtures of tris-dimethylamino-phosphine, -arsine, and -stibine with trimethylgallium, trimethylaluminum, trimethylindium and triethylgallium. The in-situ FTIR experiment is carried out in a static system, the group III and group V source are mixed into a gas cell and the evolution of gas-phase reactants and products is observed as a function of time. In the ex-situ NMR experiment, both the volatile and non-volatile by products of the reactions are analyzed to verify the IR assignments. In the case of the phosphine compound, strong acid-base interactions lead to the formation of stable and low vapor pressure products bonded between the group III atom and a nitrogen atom of tris(dimethylamino)phosphine. Similar adducts are observed for the arsine source, but in this case, the adducts decompose further to form the dimer ([R₂MN(CH₃)₂]₂, M = Al, Ga or In, R = CH₃ or C₂H₅), and dialkyl(dimethylamino)arsine [AsR₂(N(CH₃)₂)]. The rate of formation of the dimer is observed to be fastest for trimethylaluminum and the slowest for
trimethylindium, in agreement to the relative strengths of the acidity of the group III sources. Similar exchange interactions between tris(dimethylamino)stibine and the trimethyl group III sources results in the formation of the group III dimer ([R2MN(CH3)2]2) and trimethylstibine. Implications of these results for different OMCVD growth of III-V compound semiconductors are discussed.

Finally, Chapter 5 lists conclusions and summarizes recommendations for future work.
Chapter 2:

In-Situ Concentration Monitoring

2.1. Introduction

The lack of process monitoring and feedback control of input partial pressures of organometallic reagents in OMCVD leads to difficulties in reproducing run-to-run film thickness and composition. Precursors are usually introduced by flowing a measured amount of carrier gas through stainless steel containers ("bubblers") containing the organometallic reagent in liquid or solid form. The exact amount of the reactant supplied to the reactor is not measured, but it is estimated assuming saturation vapor pressure inside the bubbler and, moreover, no interactions between the reagents and the interior walls of gas handling system. Variations in source delivery are particularly acute for solid precursors, such as trimethylindium (TMIn), and low vapor pressure precursors. The change in surface area of a solid precursor during its evaporation may result in uncontrolled fluctuations in the delivery rate.\textsuperscript{10} The feed rate of a low vapor precursor from a container maintained at a higher than ambient temperature may also be affected adversely by condensation on colder sections of the gas handling system.

Current sensor technology is based on measurements of the speed of sound\textsuperscript{10} in a binary mixture of the organometallic precursor and its carrier gas. This approach has been successfully employed in monitoring of TMIn delivery\textsuperscript{11}, but the system is limited to measurement in the gas delivery system, restricted to pressures above 400 torr, and being a physical measurement, it cannot detect the
presence of different chemical species. Ultraviolet-visible (UV/Vis) spectroscopy has been shown to be a potential optical monitoring technique for direct probing of OMCVD processes\textsuperscript{12}, but photolysis reactions driven by the UV light cause difficulties with deposition on the windows of the monitoring cell.

Fourier transform infrared (FTIR) spectroscopy is a particularly useful technique for monitoring the OMCVD process since it directly probes chemical bonds and is low in energy, thus avoiding photolysis of the organometallic precursor.\textsuperscript{1,3} Recent advances in fluoride infrared fibers make it possible to expand FTIR beyond bench-top applications to remote \textit{in-situ} concentration monitoring.\textsuperscript{69} Fluoride fibers, which have > 90\% signal transmissivity over a 5 meter length, are suitable for monitoring systems with vibrational absorption bands in the 20,000-2200 cm\textsuperscript{-1} range.

In this chapter, the fiber optic based FTIR (FOB-FTIR) spectroscopy is explored for remote \textit{in-situ} organometallic concentration monitoring. The technique is based on the absorbance of organometallic reagents in the 2800-3000 cm\textsuperscript{-1} band, which corresponds to C-H vibrational stretching of alkyl groups. This frequency range is not only transparent for the fluoride fiber but also for quartz (see Figure 1.4), which is the material of choice of an OMCVD reactor. Thus, the technique will allow direct monitoring of chemical species in an OMCVD reactor. This chapter discusses feasibility studies of the technique (section 2.3), comparison of the technique with the ultrasonic measurement and implementation of the technique for looking at transient delivery of various organometallic precursors both in the gas delivery lines (2.4) and to an OMCVD reactor (section 2.5).
2.2 Experimental system and procedures

2.2.1 The fiber-optic based FTIR system

The FOB-FTIR system, supplied by Galileo Electro-Optics Corporation, is shown schematically in Figure 2.1. The spectrometer is a KVB Analect Diamond-20. The system is controlled by a Dell 486-50 MHz computer. The IR emission from the interferometer is coupled into the fibers through an optical fiber launcher. The optical fibers transport the infrared radiation to the sensing region where the light is collimated into a 12 mm beam with a prealigned optical collimator module optimized for the mid-infrared. The collimated beam passes through the gas cell and is focused into the return fiber with a second pre-aligned optical module. Angular adjustment on both collimators allows optical throughput of the system to be optimized. The light is directed to the detector box by the fiber. Two different liquid nitrogen cooled detectors were evaluated; they are: 1) a mid-IR mercury cadmium telluride (MCT) detector and 2) an indium antimonide (InSb) detector. The detector box is equipped, as well, with a computer-driven optical channel selector (OCS) that allows multiplexing among up to seven sensor points while using only one spectrometer. Three different sets of fiber systems were tried; they are a) a single fluoride fiber system with 4m total length, b) a seven-fluoride-fiber-bundle system with 4 m total length and c) a single chalcogenide fiber system with 2 m total length.

2.2.2 MIT- Crystal Specialty system

Most of the in-situ concentration monitoring results in the gas delivery system presented in section 2.4 (except 2.4.2) and gas phase decomposition
chemistry of tris-dimethylamino group V (chapter 3) experiments were performed in a Crystal Specialty OMCVD system. The system, as shown in Figure 2.1a, is equipped with a state-of-art gas handling system which is constructed of stainless steel tubing and welded VCR fittings, similar to those described earlier in section 1.2. There are three active organometallic delivery lines. Each organometallic bubbler is maintained in a temperature controlled bath. The flow rate of the carrier gas to the bubbler is metered by a precision mass flow controller. The pressure of the bubbler is monitored by a capacitance manometer. Each line is equipped as well with a run-vent switching configuration.

The growth reactor is replaced by a 12.7 cm long and 2.5 cm diameter quartz gas cell designed for concentration monitoring and probing gas-phase reactions (Chapter 3). The schematic diagram of the gas cell is shown in Figure A.1. The cell is made of a quartz tube with quartz flanges fused to both ends. Each flange is sealed by an o-ring to a stainless steel flange that contains an IR windows. The gas cell is heated by a heating tape which is wound around the tube. To maintain uniform temperature and to prevent heat loss, the gas cell is insulated in addition with a glass wool tape. The cell temperature is measured by inserting a K-type thermocouple into a well in the cell body. The pressure is measured by a capacitance manometer and is manually controlled by a precision needle valve.

The system is equipped with a mechanical vacuum pump, which provides operating pressure down to 1 torr. The exhaust gas is treated by a charcoal filter before it is released to the air.

2.2.3 Lincoln Laboratory- OMCVD System
A comparison between FTIR and the ultrasonic monitoring, described in section 2.4.2, was carried out in a Thomas Swan OMCVD growth system, which is located at Lincoln laboratory. A simplified diagram of the state-of-the-art OMCVD growth system is shown in Figure 2.1b. The ultrasonic cell (Epison) is mounted between the bubbler and the pressure controller of the organometallic source. The IR gas cell is placed in parallel with the vent line of the gas delivery system.

The *in-situ* direct concentration monitoring from an OMCVD reactor was performed in a vertical stagnation point flow reactor (Figure 2.1 b). The reactor is constructed of a quartz tube (10 cm inner diameter). From the gas handling system, the group III and group V organometallic sources are diluted with the carrier gas in a common manifold then travel through a 4 ft. length 1/4” stainless steel tubing before reaching the reactor inlet. The gas is further mixed and passed to the reactor through a stainless steel mesh flow distributor. The gas travels 15 cm before reaching the susceptor.\textsuperscript{70}

The IR concentration measurements were performed in the region between the reactor inlet and the susceptor. The total gas flow rate was 10 SLM and the reactor pressures were varied between 0.2 and 1 atm. Typical organometallic flow rates were in the range of 1 to 5 sccm. These operating conditions were similar to those used in deposition of high quality epitaxial layers.\textsuperscript{70}

Flow visualization experiments combined with fluid mechanic analysis indicate that no recirculation patterns are present and that concentrations of organometallic species are expected to be uniform across the reactor.\textsuperscript{70, 71} Under this flow condition, no deposition on the wall occurs during the growth process, except on region near the susceptor. Thus, it is possible to implement *in-situ* monitoring with the FOB- FTIR through the reactor wall.
Figure 2.1  a) Schematic diagram of FOB-FTIR set-up for in-situ monitoring of gas phase organometallic species and the Crystal Specialties OMCVD system 
b) Schematic diagram of the Lincoln Laboratory OMCVD set-up and the FOB-FTIR.
2.2.4 Chemical/ organometallic sources

Ultra-high purity H\textsubscript{2} (99.9995\%) from Matheson is used as a carrier gas. 99.5\% D\textsubscript{2} (Matheson) and 99.9995\% He (Airco / Matheson) are used for gas phase chemistry study. One percent CH\textsubscript{4} in N\textsubscript{2} (Aldrich Chemicals) is used to calibrate and test the monitoring system. Trimethylgallium (TMG), trimethylaluminum (TMAI) and triethylgallium (TEG) are obtained from Texas Alkyl. Tertiarybutylphosphine (TBP), tertiarybutylarsine (TBAs), tris-dimethylaminoarsine, phosphine and stibine (DMAP, DMAAs and DMASb respectively) and trimethylindium (TMIn) are from by Air Products and Chemicals. Tertiarybutylaluminum (TTBAI) is supplied by Epichem Ltd. Trimethylantimony and triethylantimony are supplied by Morton International.

2.3 Detection limits of the FOB-FTIR systems

In the FTIR technique, the concentration of an organometallic precursor is linearly related to the absorbance at a given wavenumber according to Beer's Law as described in Section 1.4. The FTIR monitoring system for inlet concentrations was tested by flowing a calibrated amount of 1\% CH\textsubscript{4} mixture in nitrogen. The concentration of the CH\textsubscript{4} is varied by changing the total pressure of the gas-cell, and its concentration is determined from the ideal gas law. The experiments were performed using chalcogenide fibers, a liquid nitrogen cooled MCT detector and CaF windows.

Figure 2.2 shows the absorbance of methane at 1304 cm\textsuperscript{-1} as a function of concentration. Each symbol in the graph represents a set of measurement. The data from three experimental runs are highly reproducible, and the linear regression fit indicates that the data follows Beer's law with a correlation
coefficient close to one. The CH$_4$ concentration is low enough that pressure broadening is not a significant effect.$^{13}$ Based on the determined slope of the line, the IR monitoring set up can be used for measuring the inlet concentration of an unknown amount of CH$_4$.

The absorption spectra of TMG at 2700-3100 cm$^{-1}$ is shown in Figure 2.3a for different TMG partial pressures realized by changing the gas cell total pressure for flow of a constant molar mixture of TMG and hydrogen. Figure 2.3b shows the corresponding absorption intensity at 2918 cm$^{-1}$ and the integration of absorbance from 3100 to 2725 cm$^{-1}$ as a function of the TMG partial pressures determined from TMG vapor pressure data.$^{3}$ Both the intensity and the absorbance area vary linearly with TMG partial pressure in agreement with Beer's Law. From the slope of the absorbance line, the absorptivity of TMG is estimated.

The minimum detection limit may be determined by taking into account the background noise. The level of noise is determined not only by the detector type but also the strength of the signal received by the detector. This is primarily a function of how efficient the light is coupled into and out the infrared fiber and the length of scan time. Longer scan times are required to reduce the noise level, however, for on-line process monitoring, short scan times are preferable.$^{72}$ These two parameters determine the optimal performance of the system.

An earlier set-up using single fluoride fibers and an MCT detector suffered from significant signal loss due to inefficiency in coupling and resulted in relatively low signal to noise level. Long scan times ($>>$ 1 min) were required to reduce the noise level down to 0.001 absorbance unit. An order of magnitude noise reduction was achieved by replacing the single fiber system with a bundle of seven fluoride fibers. The scan time was reduced to 15 s with the same noise level of 0.001.
Figure 2.2  Methane absorbance at 1304 cm\(^{-1}\) versus concentration.
Figure 2.3  

a) FTIR spectra for TMG at different partial pressures.

b) Intensity of TMG absorption at 2918 cm$^{-1}$ and peak intensity versus partial pressure at 40°C.
Additional improvement in the detection limit was achieved by replacing the MCT detector with a more efficient InSb detector. Table 2.1 summarizes the noise level as a function of different scan times for the set-up. As an example, a noise level of \( \leq 0.001 \) is achieved using a 1 second scan time. Based on the 0.001 noise level and a 10 cm IR pathlength, the threshold limit for TMG concentration monitoring is approximately 0.05 torr at room temperature. This short scan time and detection level are promising for further OMCVD applications of the FTIR monitoring technique since the limit represents only about < 0.5 % of typical partial pressures of TMG used in gas handling systems. Further improvements are possible; for example, the signal could be enhanced by increasing the path length of the infrared radiation through the use of multiple reflections.

Table 2.1 Comparison of the noise level obtained from the set-up using the InSb detector and the seven fluoride fibers bundle.

<table>
<thead>
<tr>
<th>Scan time (sec.)</th>
<th>Number of Scans</th>
<th>Noise level* (a.u.)</th>
<th>Noise Level** (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>&lt; 0.001</td>
<td>0.0005</td>
</tr>
<tr>
<td>6</td>
<td>16</td>
<td>0.0003</td>
<td>0.0002</td>
</tr>
<tr>
<td>20</td>
<td>64</td>
<td>0.0001</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>

* Based on transmission through two quartz windows
** Based on straight transmission (no windows)

By using a similar approach described for TMG, absorptivity has also been obtained for TTBA1, TMIn, TEG, TBP, TESb, TMSb, DMAP, DMAAs and DMASb and the results are summarized in Table 2.2. The wavenumber used for each of the absorption measurements corresponds to the maximum peak intensity. As
expected, the absorptivity increases with the number of C-H bonds in the molecule, leading to a corresponding improvement in the detection limit; e.g., it reduces to a partial pressure of 0.006 torr for DMAP.

For the set-up with the InSb detector and the seven fluoride fiber bundle system, further reduction in the noise level to 0.0001 absorbance unit can be achieved by increasing the scan time to 20 seconds. These significant improvements permit direct in-situ probing of chemical species in an OMCVD reactor, in which the organometallic concentration is typically two orders of magnitude lower than that in the delivery line. For example, in the Lincoln Laboratory OMCVD reactor system typical group III organometallic concentrations used for the growth is ≥ 100 ppm. For TEG, this concentration is significantly larger than minimum detection limit, which is 3 ppm at atmospheric pressure and 15 ppm at 0.2 atm. FOB-FTIR probing organometallic concentrations in the OMCVD growth system are further discussed in Section 2.5.

The low noise level of the InSb detector also permits direct probing of AsH₃ species in the reactor via absorbance of overtone vibration modes at around 3100 cm⁻¹. Figure 2.4 shows the spectrum of AsH₃ at 10,000 ppm concentration under atmospheric conditions. This level of AsH₃ concentration is typically used for epitaxial growth of AlGaAs materials. This technique is promising as well for measurement of other hydride sources such as NH₃ which has a strong N-H stretching absorbance at 3400 cm⁻¹ and PH₃ which also has absorbance at around 3400 cm⁻¹.
Table 2.2  Peak positions, absorptivity and detection limits for selected organometallic precursors.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Peak Position (cm(^{-1}))</th>
<th>Number of C-H Bonds</th>
<th>Absorptivity (cm(^2)/molecule)</th>
<th>Detection Limit** (torr at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMG</td>
<td>2918</td>
<td>9</td>
<td>(7.8 \times 10^{-20})</td>
<td>.05</td>
</tr>
<tr>
<td>TEG</td>
<td>2954</td>
<td>15</td>
<td>(19 \times 10^{-20})</td>
<td>.02</td>
</tr>
<tr>
<td>TMIn</td>
<td>2926</td>
<td>9</td>
<td>(7.9 \times 10^{-20})</td>
<td>.05</td>
</tr>
<tr>
<td>TTBAI</td>
<td>2846</td>
<td>27</td>
<td>(50 \times 10^{-20})</td>
<td>.006</td>
</tr>
<tr>
<td>TBP</td>
<td>2299</td>
<td>*</td>
<td>(31 \times 10^{-20})</td>
<td>.008</td>
</tr>
<tr>
<td>TBP</td>
<td>2957</td>
<td>12</td>
<td>(28 \times 10^{-20})</td>
<td>.009</td>
</tr>
<tr>
<td>TMSb</td>
<td>2991</td>
<td>9</td>
<td>(6.9 \times 10^{-20})</td>
<td>.06</td>
</tr>
<tr>
<td>TESb</td>
<td>2958</td>
<td>15</td>
<td>(23 \times 10^{-20})</td>
<td>.02</td>
</tr>
<tr>
<td>DMAP</td>
<td>2789</td>
<td>18</td>
<td>(46 \times 10^{-20})</td>
<td>.006</td>
</tr>
<tr>
<td>DMAAs</td>
<td>2787</td>
<td>18</td>
<td>(34 \times 10^{-20})</td>
<td>.007</td>
</tr>
<tr>
<td>DMASb</td>
<td>2784</td>
<td>18</td>
<td>(34 \times 10^{-20})</td>
<td>.007</td>
</tr>
</tbody>
</table>

* P-H vibrational stretching.

** Based on 0.001 noise level in the system.
Figure 2.4  Infrared spectrum of 1% AsH$_3$ in the Lincoln Laboratory OMCVD reactor at 1 atm.
2.4 In-situ monitoring in the gas delivery system

2.4.1 In-situ monitoring of delivery transients

The utility of the FTIR technique in following species concentrations and detecting potential organic impurities is demonstrated in two examples: (i) turn-on/-off transients for a TMG bubbler, and (ii) long-term fluctuations in TMIn delivery rates. The measurements were carried out using a single fluoride fiber system, an MCT detectors and CaF$_2$ windows. Figure 2.5a shows the spectral evolution during turn-on of a TMG bubbler that has been stored for two months at -10°C. The gas cell pressure was maintained at 600 torr as a 60 sccm hydrogen flow was established through the bubbler and the by-pass line was closed. A narrow peak at 3016 cm$^{-1}$ attributed to methane is present initially, while the characteristic signature of C-H stretching vibrations of TMG at 2918 cm$^{-1}$ dominate at later times.

The results of deconvolution of the TMG and methane peaks are summarized in Figure 2.5 b. The methane partial pressure peaks at a maximum value at about 2 min and then decays slowly with time. The TMG partial pressure reaches a steady state concentration after 5 min. After 16 min, when the hydrogen flow is switched from the bubbler to the by-pass line, the TMG and methane signals rapidly decrease to zero. A similar experiment repeated after 30 min reveals a faster approach of the TMG concentration to steady state and no detectable methane (Figure 2.3b). A third run performed immediately after the second run produces essentially the same transient as the second run, indicating that the TMG vapor pressure inside the bubbler has been stabilized.
Figure 2.5  
a) Evolution in FTIR spectra during startup of a TMG bubbler not having been used for 2 months.

b) Partial pressures at TMG and methane as functions of time, (•): TMG (run 1); (x): methane (run 1); (O): TMG (run 2). The supply of TMG was turned off at 16 min.
Figure 2.6  Temporal variation in TMIn partial pressure for constant bubbler temperature (40°C).
The formation of methane, also observed in TMIn containers stored for long periods of time, is probably caused by decomposition of the alkyl in the presence of small amounts of moisture which is adsorbed on tube walls and unintentionally introduced during a bubbler change. The presence of small amounts of methane, a stable hydrocarbon at growth conditions, will not affect the properties of the grown layers. However, the presence of the gas could influence the accuracy of the concentration measurements based on the speed of sound in the mixture, as it is discussed in the next section. Figure 2.6 illustrates the use of the infrared detection scheme in monitoring typical long-time scale variations in TMIn partial pressure. These fluctuations are attributed to TMIn being a solid source with a changing surface area for evaporation.

2.4.2 A comparison of the FTIR and the ultrasonic techniques

The performance of the FTIR measurement is compared to that of the ultrasonic technique for the delivery of a promising new aluminum source, tri-tertiarybutylaluminum (TTBAI). The vapor pressure was not known prior to this study. The pressures of the bubbler and the ultrasonic cell were kept at 800 torr, while the FTIR gas cell was kept at atmospheric pressure. Total carrier gas flow was 350 sccm. The bubbler temperature was at 25°C while the ultrasonic cell and line temperatures were kept uniformly at 50°C. The IR gas cell was kept at 90°C to minimize condensation.

Figure 2.7 shows the transient of TTBAI partial pressure measured by the ultrasonic technique for a newly received bubbler. The measured pressure continues to decrease even after the carrier gas was flowed for more than 5 hours. The continual decrease of the signal indicates the presence of foreign gas species in the bubbler.
The transient infrared spectra during TTBAI delivery from a newly received bubbler is shown in Figure 2.8a. The spectra at earlier times show strong and distinguishable peaks at 3089, 2967 cm\(^{-1}\) which decay as a function of time. In contrast, the 2847 cm\(^{-1}\) peak increases as a function of time. The spectra continues to change even after hydrogen has flowed through the bubbler for more than 1 hour.

Figure 2.8b shows another transient delivery spectra after the bubbler is used for several growth runs. The ratio of peak at 2967 to 2847 cm\(^{-1}\) shows a decrease as a function of time until steady state was obtained at 21 min. This observation suggests volatile species are present at the beginning of the transient and became depleted with time.

Analysis of spectra for the transient shown in Figure 2.8a, indicates the presence of isobutene and isobutane along with TTBAI.\(^{75}\) The appearance of isobutene is evidenced by the observation of the peak at 3089 cm\(^{-1}\) and isobutane is identified by the appearance of sharp peak at 2967 cm\(^{-1}\). It is likely that isobutene and isobutane observed in the transient are the product of decomposition of TTBAI in the bubbler, similar to appearance of methane during the transient of TMG and TMIn (section 2.4.1).

Figure 2.9 shows the results of deconvolution of FTIR spectra for isobutane, isobutene and TTBAI corresponding to the transient delivery in Figure 2.8b. The initial transient shows a trace amount of isobutane and isobutene. The TTBAI signal continues to increase until a steady state is reached. The figure also includes the ultrasonic measurement, which shows a sharp increase in the signal at the beginning of the transient. The spike is caused by the presence of the hydrocarbon gases which changes the speed of sound measurement (equation 1.7). Vapor pressure data were extracted from the ultrasonic measurement when the FTIR confirmed that only TTBAI was present in the mixture. Assuming that
the specific heat of TTBAI is similar to those used in TMIn and TMG\textsuperscript{10}, the vapor pressure of TTBAI at 24°C is determined to be 0.5 torr. The TTBAI absorptivity at 2846 cm\textsuperscript{-1} is determined by assuming this vapor pressure.

The utility of having a chemically selective on-line sensor, such as FTIR, is illustrated for the detection of low vapor pressure impurities. Figure 2.10 compares the steady state spectra from two TTBAI sources. The top is obtained from a non-electronic grade source, while the bottom spectrum is from an electronic grade source. The presence of impurities in the non-electronic grade source results in increase in the ratio of peak heights at 2967 cm\textsuperscript{-1} and 2847 cm\textsuperscript{-1}. Spectral analysis of the non-electronic grade spectra shows that the difference is from absorbance of CH\textsubscript{3} stretching of isoctane (shown in the inset of Figure 2.10). \textit{Ex-situ} NMR analysis of both samples confirmed this assignment. This hydrocarbon species has a relatively low vapor pressure and remained in the bubbler even after the bubbler was purged with hydrogen for over 20 hours. This impurity results in about 5 to 10 % higher value of concentration reading from the ultrasonic measurement. Similar problems with hydrocarbon impurities could be observed as well during delivery of other organometallic sources, such as trimethylaminealane and triisobutylaluminum, which are reported to decompose in the bubbler under long term storage.\textsuperscript{25}

Another advantage of the FTIR technique compared to the ultrasonic measurement is the range of operating pressures. The ultrasonic measurement is restricted to operation $\geq$ 400 torr, whereas the FTIR measurement is only dependent on the partial pressure of the organometallic source.
Figure 2.7 Transient monitoring of TTBAI concentration using the ultrasonic measurement for delivery from a new TTBAI bubbler.
Figure 2.8  FTIR spectra of transient delivery from a) a new TTBAI bubbler, b) the same bubbler after the bubbler was used for several turn-on/ turn off experiments.
Figure 2.9  Comparison between the FTIR and the ultrasonic measurement. Three species were detected by FTIR: TTBAI, isobutane and isobutene.
Figure 2.10  Comparison between the steady state spectra during delivery from two TTBAI bubblers, the top spectra is from a non-electronic grade source, the bottom spectra is from an electronic grade source.
2.4.3 Effects of condensation and precursor-wall interactions.

The temporal variation in precursor concentration during bubble startup and shutdown may be utilized as a tool for detecting possible precursor interactions with the walls of the gas handling system. Under typical OMCVD conditions the gas flow in the stainless steel tubing may be characterized as "plug flow".\textsuperscript{76} This behavior implies that a change in concentration of the organometallic precursor made by switching the flow on or off to the bubbler, results in a time lag, \( \tau_L \), before the signal is detected by the gas cell measurement. \( \tau_L \) is related to the length of the gas line \( (L) \) between the bubbler and the cell and the gas velocity, \( v \), in the tube according to:

\[
\tau_L = \frac{L}{v}. \tag{2.1}
\]

The flow in the gas cell will, on the other hand, be representative of a well-mixed system\textsuperscript{76} because of the cell geometry and the low flow rate relative to diffusion time. In that case the species balance for the organometallic precursor takes the form:

\[
\frac{\partial c}{\partial t} = \frac{1}{\tau_c} (c_{in}(t) - c) \quad \text{[gas cell].} \tag{2.2}
\]

Here \( c \) is the precursor concentration in the gas cell as a function of time \( t \); \( c_{in}(t) \) is the concentration of organometallic precursor coming into the gas cell, and \( \tau_C \) is the residence time of the gas cell (volume/volumetric flow). In the absence of wall interaction and at steady state, \( c_{in}(t) \) is essentially constant and equal to the precursor concentration in the bubbler \( (c_0) \). The solution to (3) with the initial
conditions $c_{in} = 0$ for $0 < t < \tau_L$ and $c_{in} = c_0$ for $t \geq \tau_L$, gives the observed concentration time behavior:

\begin{align}
  c(t) &= 0 & 0 \leq t < \tau_L, \\
  c(t) &= c_0 \left[ 1 - \exp \left( - \left( \frac{t - \tau_L}{\tau_c} \right) \right) \right] & t \geq \tau_L.
\end{align}

The turn-off transient, having a similar functional form $c(t)$ remains at the steady state value for a length of time $\tau_L$ and then decreases exponentially. Because of this similarity in transients, data may be fitted to the same master response curve based on Eqn. 2.4. Data from the equilibrated TMG bubbler experiments shown in Figure 2.5 (runs 2 and 3), do indeed fit the same functional form (shown in Figure 2.11). Furthermore, the model predicts the time lag($\tau_L$) and the residence time ($\tau_c$) within the experimental accuracy. This good agreement between predicted and observed dynamic response implies that the delivery of TMG is not influenced by artifacts; in particular, condensation in the gas line or adsorption on gas cell walls and windows.

The presence of precursor wall interactions will influence the inlet concentration of $c_{in}(t)$ as a function of time and will produce long transients and seemingly irreproducible variations in steady state precursor concentrations. The effect of precursor-wall interactions on precursor delivery may be quantified through the following mathematical model.

Again, assuming plug flow, the mass balance for the organometallic species in the gas line now takes the form:

$$v \frac{\partial c_L}{\partial x} + \frac{\partial c_L}{\partial t} + \frac{\partial n}{\partial t} = 0,$$

(2.5)

where $c_L$ is the concentration in the gas line and $n$ is the concentration of the
surface species expressed per unit volume of the gas line. The third term represents the interaction between the gas phase and the surface species. Since the precursor is usually diluted in a carrier gas, this interaction may be assumed to be linear:

\[
\frac{\partial n}{\partial t} = k_1 c_L - k_2 n .
\]  

(2.6)

Here, \( k_1 \) and \( k_2 \) are the rate constants for absorption and desorption of the molecule, respectively. The physical situation is mathematically equivalent to simulating chromatography of a single solute, a well-studied problem. Assuming that the interaction is uniform along the length of the delivery line, the solution for a step increase in concentration in the inlet of the gas cell at a time greater than \( \tau_L \) is:

\[
c_{in}(t) = c_0 [1 - e^{k_2(t - \tau_L)}] \int_0^{k_1 \tau_L} e^{-s} I_0(2\sqrt{k_2(t - \tau_L)s}) ds ,
\]

(2.7)

where \( I_0(s) \) is the modified Bessel function of zero order. For the case where no organometallic species is present initially, the solution for the gas cell concentration takes the form:

\[
c(t) = \frac{1}{\tau_c} e^{-\frac{(t - \tau_L)}{\tau_c}} \frac{t - \tau_L}{\tau_L} \int_{\tau_L}^{\tau_c} e^{-\frac{t - \tau_L}{\tau_c}} c_{in}(t) dt \quad t \geq \tau_L.
\]

(2.8)

This result may be used to gain insight into temporal reactions of precursor partial pressures when wall interactions occur. Using the experimentally determined values for \( \tau_L \) and \( \tau_c \), Figure 2.12 illustrates possible precursor transients for different values of the rate constants \( k_1 \) and \( k_2 \). If adsorption takes place with no desorption (\( k_1 \neq 0 \) and \( k_2 = 0 \)), the net effect is to reduce the steady
state concentration of the precursor (curve A). When redesorption occurs at a relatively slow rate (curve B), the concentration varies slowly over the typical time scale for bubbler equilibrium. A larger desorption rate allows for a faster approach to the steady state (curve C). Reduced adsorption rate lowers the steady state offset (curve D). In the limit of no adsorption/condensation \((k_1 = 0)\), or very fast desorption \((k_2 >> 1)\), the transient behavior is as observed for TMG and predicted by Eqn. (2.5) (curve E).

Experimental examples of precursor transients displaying the influence of wall interactions are shown in Figures 2.13a and b for TMIn and DMAP, respectively. Turn-on and -off transients are illustrated for three increasing temperatures of the gas line and monitoring cell, 25°C, 40°C and 60°C. The bubbler temperature was kept constant at 40°C for each of these experiments so that the partial pressure of the precursor in the bubbler remained constant. Under these conditions the concentration in the gas cell would be expected to decrease with temperature because of the gas expansion. However, the actual transients display the opposite behavior. The steady state concentration increases significantly with gas line and cell temperature. This seemingly contradictory observation may be explained in terms of condensation and wall interactions, as in the above model.

In the case of TMIn, the effect is mostly caused by condensation \((k_1 \neq 0)\). As the behavior of DMAP appears to be further complicated by a wall interaction, in particular at 25°C, resulting in a long time lag during the DMAP switch off. This time lag is probably caused by re-evaporation from the wall, similar to the memory effect reported for doping of GaAs during OMCVD with Mg, Se and Zn organometallic sources\(^7\). The effect is eliminated at high temperatures where the desorption rate \((k_2)\) is rapid.
Figure 2.11 Comparison between turn-on (O) and turn-off (X) of TMG delivery transients. The solid curve represents the model using $t_c = 42$ sec. and $t_L = 25$ sec.
Figure 2.12  Simulated startup transients for systems with wall interactions. A: $k_1 = 0.2 \text{ s}^{-1}$, $k_2 = 0$; B: $k_1 = 0.2 \text{ s}^{-1}$ and $k_2 = 0.1 \text{ s}^{-1}$; C: $k_1 = 0.2 \text{ s}^{-1}$ and $k_2 = 0.6 \text{ s}^{-1}$; D: $k_1 = 0.0667 \text{ s}^{-1}$ and $k_2 = 0$; E: no condensation ($k_1 = 0$) or fast desorption ($k_1 >> 1$).
Figure 2.13  a) TMIn delivery transient at gas line temperatures: 25°C (O), 40°C (•) and 60°C (X).  b) DMAP delivery transient at gas line temperatures of 25°C (X), 40°C (O) and 60°C (Δ). The arrows indicate the time the organometallic flow was switched off. The organometallic sources were maintained at 40°C in all cases.
2.5 Direct *in-situ* monitoring in an OMCVD reactor

2.5.1 Determination of the stability of organometallic delivery from a bubbler at different flow and pressure conditions

The FOB-FTIR system with the InSb detector and the seven-fluoride-fiber bundle system, is demonstrated for *in-situ* steady state measurement of organometallic delivery as a function of different carrier gas flow rates and bubbler pressures. The purpose is to determine whether the vapor pressure of the organometallic is constant over a wide range of experimental parameters. In the first study, the delivery of triethylantimony (TESb) was investigated under carrier gas flow rates of 0 to 500 sccm, and three different bubbler pressures of 200, 400 and 800 torr. The bubbler was kept at 25°C and the reactor pressure was at 0.2 atm. Figure 2.14 shows the plot of absorbance as a function of calculated deliveries assuming saturation condition inside the bubbler. The three symbols in the graph represent the three bubbler pressures. Least square analysis shows that the data is linear with correlation coefficient equal to 1.000, indicating the vapor "pick up" was constant under the conditions investigated.

Similar experiments were carried out as well for TMIn. The bubbler pressure was maintained at 800 torr, the reactor pressure was at 1 atm and carrier gas flow was varied from 0 to 500 sccm. The bubbler was kept at 25°C and the flow of carrier gas to the bubbler was reversed to maximize the evaporation of the organometallic precursor. For comparison, the concentration of TMIn was measured as well with the ultrasonic technique.

Figure 2.15 summarizes the results. The absorbance data of TMIn (X) is plotted against the flow rate of carrier gas to the bubbler. The delivery data from the ultrasonic measurement (circles and the dashed line) are also compared in
the same plot. The solid line represents the calculated TMIn delivery rates assuming complete saturation in the bubbler. The data show good agreement between both the FTIR and the ultrasonic measurements. The discrepancy between the measurements and the calculated data suggests that the bubbler is not under saturation condition. At higher flow rates, the vapor pick up decreases and results in a significant decrease in TMIn delivery. This problem is commonly observed for TMIn bubblers which have not been used for a long period of time.

2.5.2 Monitoring interactions between group III and V sources

Interactions between organometallic sources in the mixing zone of the reactor can reduce the OMCVD growth performance. In this section, the FOB-FTIR is used to gain insight into the effect of Lewis acid-base interactions in OMCVD growth of III-V materials using TTBAI and arsine, TTBAI and TMSb, and TTBAI and TESb.

The experiments were performed in the OMCVD reactor at Lincoln Laboratory shown schematically in Figure 2.1b. The monitoring experiments were carried out under flow and pressure conditions similar to those used for film growth. The spectra in Figure 2.16a are for a mixture of 0.7 sccm TTBAI and 7 sccm AsH₃ (V/III = 10), while the spectra in figure 2.16b correspond to the mixture with V/III = 100 using the same amount of group III source.⁷³ For the V/III = 10, no apparent interaction is observed since the spectra of the mixture (solid line) and TTBAI (dashed line) are identical. On the contrary, for V/III = 100, the mixture spectrum shows an increase in absorbance due to wall condensation. These interactions were observed after the mixture had been delivered to the reactor over 5 min. The earlier spectra did not show evidence of
interactions. This wall deposit evaporated as the wall temperature was increased to 50°C. To prevent this adduct condensation, which could be parasitic for OMCVD growth, the reactor wall should be kept at temperature greater than 50°C.

Interaction between TTBAI and TMSb produced gas phase adducts. The solid line in Figure 2.17a is the spectrum of the mixture of 0.7 sccm TTBAI and 4 sccm of TMSb. The spectrum is compared to the dashed line spectrum which is obtained by addition of the individual spectra of 0.7 sccm TTBAI (bottom) and 4 sccm TMSb (middle). Evidence of the Lewis acid-base interaction is distinguished by the emergence of a broad shoulder band around 2830 cm⁻¹. The vapor phase adducts were transported to the reactor. The interaction decreased as the concentrations of the organometallics were reduced. For example in figure 2.17b, by reducing the group V species to 2 sccm while maintaining the same group III flow, less interaction is observed. As pointed out in Section 1.8, the formation of gas phase adducts should not affect the overall chemistry of the growth process. The adducts bond is relatively weak and should break as the adducts reach the high temperature regime of the reactor. However, if adducts condensation occurs in the mixing zone, a lower growth rate and higher impurities incorporation could result. The condensation in fact is observed for the mixture of TTBAI and TESb.

The solid line in figure 2.18a is the spectrum of the mixture of 0.5 sccm TTBAI and 1 sccm of TESb. The mixture spectrum is lower compared to the addition spectrum (dashed line), indicating reduce organometallic supply to the reactor due to condensation of Lewis acid-base adducts.
Figure 2.14 TESb absorbance as a function of calculated TESb flow assuming saturation conditions inside the bubbler.
Figure 2.15 TMIn absorbance (X) as a function of hydrogen flow rate for the bubbler held at 800 torr. The TMIn flow rate that is based on the ultrasonic reading (--O--) and calculated with the assumption of complete saturation(—) are plotted in the same graph.
Figure 2.16 Comparison between infrared spectra of TTBAI (----) and a mixture of TTBAI and arsine (—) for: a) V/III = 10 and b) V/III = 100.
Figure 2.17  Infrared spectra of TTBAI and TMSb mixture a) for V/III = 5.7 and b) for V/III = 2.8. Each graph shows the spectra of TTBAI (bottom), TMSb (middle) and mixture of TMSb and TTBAI (top). The dashed line is the result of addition of TTBAI and TMSb spectra.
In-situ monitoring during turn-on and -off of TTBAI and TESb flow into the reactor was performed and the results are summarized in figure 2.18 b. The spectrum immediately taken after the flow was switched in at 0.25 min shows mostly excess TESb, which is characterized by triplets peaks at 2956, 2917 and 2884 cm\(^{-1}\), and the adduct peak from TTBAI at 2864 cm\(^{-1}\). The adduct peak increased as a function of time indicating possible adducts re-evaporation.

Stronger evidence of adduct re-evaporation is observed during turn-off experiment. Both TTBAI and TESb flows were switched off at 6 min and the reactor was continuously purged with hydrogen. The spectrum collected at 6.5 min shows increased in gas phase Lewis acid-base adducts between TTBAI and TESb. The adducts were observed during the span of 9 min after shut off.

The adducts condensation and re-evaporation process is consistent with the AlSb OMCVD growth observation in the same reactor. The AlSb growth process was carried out at 550° C under the same operating pressure (150 torr) using 1 sccm of TTBAI and 1.8 sccm of TESb for an hour. At the end of the growth process, a thin cap layer of GaSb film was grown on top of the AlSb film using triethylgallium (TEG) and TESb. The interaction between TTBAI and TESb produces solid white deposits in the mixing zone of the reactor. This interaction affects the film composition. Auger depth profile of the film, as shown in Figure 2.19, indicates that aluminum is incorporated into GaSb cap layer and continues to be deposited even after all the sources have been switched off from the reaction zone during substrate cool down. The source of aluminum, in this case is the re-evaported adduct from the wall of mixing zone. The low decomposition temperature of TTBAI (see Appendix A.3) and the relatively high substrate temperature cause the post aluminum deposition.
Figure 2.18  a) *In-situ* FOB-FTIR spectra of TTBAI and TESb mixture is for \( V/III = 2.0 \) The spectra of TTBAI (bottom), TESb (middle) and mixture of TMSb and TTBAI (top). The dashed line is the result of addition of TTBAI and TESb spectra.

b) Transient spectra during turn on and off of flow of TTBAI and TESb mixture (\( V/III=2.0 \)) to the reactor.
Figure 2.19  Auger depth profile analysis of multilayer AlSb-GaSb films grown using combination of TEG, TTBAI and TESb.
2.6 Summary

FOB-FTIR spectroscopy is a useful technique for monitoring partial pressures of organometallic precursors that are introduced to an OMCVD reactor and for direct concentration monitoring in an OMCVD reactor. The technique is based on absorption of infrared radiation in the range of 5000 - 2400 cm$^{-1}$ by molecular vibrations, which is linearly related to the concentration of organometallic precursor in the sampling path. The C-H vibrational stretching bands are particularly useful since they are strong and found in all alkyl sources. The far infrared region (600-100 cm$^{-1}$), in principle, could be used to monitor metal-carbon bands and thus distinguish among different alkyl sources. However, spectroscopy in this region is generally more difficult because of low intensity of IR sources and lack of low loss fiber materials. For on-line monitoring in the gas delivery system, typical detection limits for a one second sampling time with a 10 cm pathlength range from 0.05 to 0.005 torr. This is significantly lower than the vapor pressure of organometallic sources used in OMCVD (> 1 torr). Improved detection limits can be achieved by increasing the scan time, and allows direct monitoring of organometallics and hydride species from a growth reactor. The chemical selectivity of the FTIR technique gives accurate measurement of the organometallic sources and allows detection of delivery problems caused by the presence of foreign chemical species, chemical interactions and fluctuations in vapor pick up from a bubbler. Simple residence time models may be used in conjunction with the FTIR technique to identify problems of wall condensation and chemical interactions.
Chapter 3:

\textit{In-Situ} Gas Phase Decomposition of Trisdimethylamino Compounds

3.1 Introduction

Significant efforts have been expanded in the development of organometallic sources for replacement of arsine and phosphine in organometallic chemical vapor deposition (OMCVD) of III-V compound semiconductors for optoelectronic applications.\textsuperscript{1,2,3} Safety concerns over the use of high pressure, toxic hydride sources have motivated research on low vapor pressure liquid organometallic sources, such as mono-tertiarybutylarsine and -phosphine. There has also been interest in organometallic antimony sources for low temperature growth of Sb containing compound semiconductors, which often are highly temperature sensitive.\textsuperscript{3,25} The wide-range organometallic reagents explored in OMCVD growth and thermal decomposition studies have been reviewed by Stringfellow,\textsuperscript{3} and more recently, by Jones.\textsuperscript{25} Briefly, two primary categories of reagents have been investigated: trialkyl sources (e.g., trimethylarsenic, triethylarsenic, trimethylphosphorus, triisopropylantimony) and alkyl hydride sources (e.g., mono-tertiarybutylarsine, mono-phenylarsine, mono-tertiarybutylphosphine).

\textit{Tris}-dimethylaminoarsine (DMAAs), \textit{tris}-dimethylaminophosphine (DMAP) and \textit{tris}-dimethylaminostibine (DMASb) represent a new family of reagents for growth of compound semiconductors.\textsuperscript{56} These reagents are
distinct from previously studied organometallic compounds due to their lack of direct group V - carbon or hydrogen bonds, and the presence of group V-nitrogen bonds. The molecules have been designed to circumvent problems of carbon incorporation often encountered in growth with trialkyl sources. They are also expected to have a relatively low decomposition temperature because of the weaker strength of the group V atom bond to nitrogen, as compared to the bond to carbon.\textsuperscript{57} OMCVD of GaAs with TMG and DMAAs in the temperature range 550-700°C has been reported by Zimmer \textit{et al.} \textsuperscript{62} No nitrogen incorporation was detected in GaAs grown at 650°C, while AlGaAs grown at 700°C appeared to be contaminated by nitrogen.\textsuperscript{58} InP films grown by using trimethylindium (TMIn) and DMAP were specular, with no detectable nitrogen or carbon incorporation.\textsuperscript{58} Low temperature growth of InSb with TMIn and DMASb, without significant impurity incorporation, has been reported as well.\textsuperscript{63, 64} The mechanism underlying the decomposition of this molecule has not completely understood.

In this chapter, the gas-phase decomposition of \textit{tris}-dimethylamino reagents at OMCVD conditions is explored by using fiber optics-based Fourier transform infrared (FTIR) and molecular beam mass spectroscopy.

\section*{3.2 Experimental techniques and procedures}

\subsection*{3.2.1 FOB-FTIR spectroscopy}

The majority of the gas-phase reaction investigations were performed using the FOB-FTIR system (Galileo Electro-Optics Corporation) shown schematically in Figure 2.1a. The spectrometer itself is a KVB Analect
Diamond-20, with a resolution of 2 cm\(^{-1}\). The system is controlled by a Dell 486-50 MHz computer. The IR emission from the interferometer is coupled into an optical fiber through a launcher. The optical fiber guides the infrared radiation to the sensing region, where the light is collimated into a 12 mm beam with a prealigned optical collimator module optimized for the mid-infrared. The collimated beam passes through the gas cell and is focused onto the return fiber with a second pre-aligned optical module. Angular adjustment on both collimators allows the optical throughput of the system to be optimized. A liquid cooled, mid-IR mercury cadmium telluride (MCT) detector is used.

Two types of optical fibers were used: chalcogenide and fluoride fibers.\(^{18}\) The former type is transparent in the spectral region 900-3300 cm\(^{-1}\) with limited transmission around 2200 cm\(^{-1}\), whereas the latter has an operating window from 2200 cm\(^{-1}\) to 20000 cm\(^{-1}\).

The experiments were performed in a Crystal Specialties OMCVD reactor system. The reactor was replaced by a gas-cell designed for \textit{in-situ} monitoring of gas phase decomposition. The cell (12.7 cm long) was constructed from a quartz tube (2.5 cm diameter), with quartz flanges fused to the tube ends, (\textit{cf.} Figure A.1). CaF\(_2\) windows with viton o-ring seals were placed at each end and sealed with stainless steel flanges that could be purged to minimize window deposits during the experiments. The cell could be uniformly heated to 650\(^\circ\)C with a resistive heater wound uniformly around to the wall of the gas cell. The temperature was determined by inserting a type-k thermocouple into a thermocouple well penetrating into the gas cell.

The thermal decomposition studies were carried out at a reactor pressure of 600 Torr using H\(_2\) (Matheson, 99.9995%), He (Airco, 99.999%) and D\(_2\) (Matheson, 99%) as carrier gases. During experiments, the total flow of carrier
gas to the reactor was maintained at 60 sccm, and the flow rate of the organometallic source was kept at 12 μmol/min. After each IR absorption measurement, the gas-cell was evacuated and a reference spectrum recorded. An average of 128 scans at 4 cm⁻¹ resolution were used for each spectrum.

Heat and mass transfer analyses, described in Appendix A, showed that transport in the cell was dominated by diffusion under the conditions investigated. Residence time distribution studies at room temperature further showed that the system behaved as a well-mixed reactor (see Chapter 2). Temperature and concentration profiles could therefore be assumed uniform across most of the cell width, except near infrared windows, which were cooled to a temperature of 50°C. To interpret decomposition data, a simple two-cell reactor model was used, based on a well-mixed reactor section for the uniform temperature region, and a dead volume section for the region adjacent to the windows. This model was calibrated against published data for the pyrolysis of trimethylgallium (TMG) and trimethylindium (TMIn) as shown in Appendix A.

The gas cell was modified in the following manner to explore possible surface effects upon decomposition of the molecules. A tube of stainless steel wire cloth was inserted into the center of the gas cell to insure an open IR beam path. Effects of SiO₂ on the decomposition were studied by inserting 4 mm diameter borosilicate beads into the annular region between the gas cell and wire cloth. GaAs surface reactions were explored by inserting polycrystalline GaAs chips.

3.2.2 Molecular beam mass spectrometer investigations
The FTIR investigations were augmented by pyrolysis studies in a stagnation point OMCVD flow reactor equipped with molecular beam sampling through a pinhole in the substrate heater. This system has been used previously in decomposition studies of different organometallic reagents.\textsuperscript{79} The gas was sampled through a 100 µm pinhole in stainless steel foil in the center of a heated graphite susceptor. The sampled gas stream was expanded into a molecular beam through two differentially pumped stages, and collimated by a skimmer towards a Balzers 311 quadrupole mass spectrometer. This arrangement emulated conditions in a growth reactor and enabled \textit{in-situ} monitoring of gas-phase species in the reactor with minimal downstream gas-phase and wall interactions. Additional details about the system have been reported previously.\textsuperscript{79}

The mass spectroscopy pyrolysis studies of the dimethylamino reagents served to verify and to complement results obtained by the infrared technique. The system played a special role in identification of decomposition products, with infrared signatures in the infrared region below 1000 cm\textsuperscript{-1}, which could not be accessed in the fiber optics-based FTIR setup. The pyrolysis studies were conducted with H\textsubscript{2} as a carrier gas, at a flow rate of 20 sccm. The reactor was maintained at 30 Torr; the delivery rate of the organometallic reagents was set at 20 µmol/min.

\textbf{3.2.3 Organometallic sources}

DMAP, DMAAs and DMASb, (Air Products and Chemicals) were electronic grade and supplied in stainless steel bubblers. The vapor pressures at the bubbler temperature of 40°C, were 6.9 Torr, 5 Torr and 4.0 Torr for DMAP, DMAAs, and DMASb, respectively. Ultra-high purity H\textsubscript{2} (99.9995%)
from Matheson is used as a carrier gas. 99.5% D₂ (Matheson) and 99.9995% He (Airco/ Matheson) are used for gas phase chemistry study.

3.3 Results

3.3.1 Decomposition of DMAAs

Typical mass spectra of DMAAs in H₂ carrier gas at 30 Torr are shown in Figure 3.1. for two different temperatures: T = 50°C, where no decomposition has occurred, and T = 450°C, after the decomposition has been completed. The low temperature spectrum displays a peak at m/e = 207, corresponding to the parent molecule; a peak at m/e = 163, representing [(CH₃)₂ N]₂ As⁺, and at m/e = 120, corresponding to [(CH₃)₂ N] AsH⁺. The fragmentation pattern of DMAAs is similar to that reported for DMAP.\textsuperscript{80} Table 3.1 gives the characteristic peaks for the three tris-dimethylamino reactants.

At the high temperature, the parent peaks at m/e = 207, 163 and 120 disappear and no products of with m/e > 75 appear except for a peak at m/e = 150, corresponding to As₂. This behavior indicates that the DMAAs decomposes cleanly to As, without the formation of any organometallic As by-products. The major products at 450°C are those of m/e = 42 and 44. The assignment of the peaks to 44 to dimethylamine, and 42 to aziridine or methylmethyleneimine, have been discussed by Salim et al.\textsuperscript{60} The peak at m/e = 15 is assigned to methyl groups originating from the fragmentation of dimethylamine, methylmethyleneimine, and methane. Further identification of the decomposition products is achieved by augmenting the mass spectroscopy data with FTIR observations.
Figure 3.1  Molecular beam mass spectra of DMAAs at a) 50°C and b) 450°C.
Table 3.1  Assignments for major peaks in DMAP, DMAAs and DMASb mass spectra

<table>
<thead>
<tr>
<th>m/e</th>
<th>DMAP Assignment</th>
<th>m/e</th>
<th>DMAAs Assignment</th>
<th>m/e</th>
<th>DMASb* Assignment</th>
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<tr>
<td>163</td>
<td>[(CH₃)₂N]₃P⁺</td>
<td>207</td>
<td>[(CH₃)₂N]₃As⁺</td>
<td>252,254</td>
<td>[(CH₃)₂N]₃Sb⁺</td>
</tr>
<tr>
<td>119</td>
<td>[(CH₃)₂N]₂P⁺</td>
<td>163</td>
<td>[(CH₃)₂N]₂As⁺</td>
<td>208,210</td>
<td>[(CH₃)₂N]₂Sb⁺</td>
</tr>
<tr>
<td>76</td>
<td>[(CH₃)₂N]HP⁺</td>
<td>120</td>
<td>[(CH₃)₂N]HAs⁺</td>
<td>165,167</td>
<td>[(CH₃)₂N]HSb⁺</td>
</tr>
<tr>
<td>60</td>
<td>[(CH₃)N]P⁺</td>
<td>104</td>
<td>[(CH₃)N]As⁺</td>
<td>120,122</td>
<td>Sb⁺</td>
</tr>
<tr>
<td>44</td>
<td>(CH₃)₂N⁺</td>
<td>44</td>
<td>(CH₃)₂N⁺</td>
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<tr>
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</tr>
</tbody>
</table>

* Sb has two significant isotopes (at m/e = 120 and 122).
FTIR spectra of DMAAs in H\textsubscript{2} at 600 Torr at three different temperatures are shown in Figure 3.2. The high temperature spectra are corrected spectra after subtracting the contribution due to the absorption in the dead volume region adjacent to the windows. The low temperature spectrum, taken at 50\textdegree C, gives the vibrational frequencies of the DMAAs molecule. The complete IR assignments for DMAAs, DMAP,\textsuperscript{81} and DMASb are summarized in Table 3.2. As the temperature of the gas cell is increased to 430\textdegree C, significant changes in the vibrational spectrum are observed corresponding to the decomposition of the molecule. As the pyrolysis proceeds, the distribution of peaks in the C-H vibrational stretching region, 2800-3000 cm\textsuperscript{-1}, loses distinct features and becomes a broad adsorption. New peaks are observed at 1600-1700 cm\textsuperscript{-1}, the peak shape at 1400-1500 cm\textsuperscript{-1} changes in appearance, and peaks at 1195 and 1250 cm\textsuperscript{-1} disappear, while the peak centered around 1155 cm\textsuperscript{-1} remains intact.

The 1155 cm\textsuperscript{-1} signature is assigned to the CH\textsubscript{3} deformation band of dimethylamine.\textsuperscript{82} Additional evidence of the presence of this product is the CH\textsubscript{3} bending mode at 1460 cm\textsuperscript{-1} (Figure 3.3). The mode for N–H stretching vibration is not detected because of its weak IR cross section.\textsuperscript{82}

The second product observed at 430\textdegree C is methylmethyleneimine. The spectra shown in Figures 3.3 and 3.4 display a sharp peak centered at 1660 cm\textsuperscript{-1} and broad shoulders at around 1676 and 1640 cm\textsuperscript{-1} stemming from the C=N stretching vibrational rotational mode of methylmethyleneimine.\textsuperscript{83} The spectra at 450\textdegree C further reveal two peaks at 1475 cm\textsuperscript{-1} and 1444 cm\textsuperscript{-1}, corresponding to the CH\textsubscript{2} and CH\textsubscript{3} bending modes of methylmethyleneimine. Vibrational modes of aziridine\textsuperscript{84} are not detected, which suggests that the m/e = 42 peak in the molecular beam mass spectrum represents the formation of methylmethyleneimine and not of aziridine.
Figure 3.2  Infrared spectra of DMAAs in H₂ at a) 200°C, b) 430°C, and c) 565°C. Spectra b is after subtracting the parents contribution.
Figure 3.3 Infra-red spectra of decomposition products of DMAAs in a) H2, b) He, and c) D2.
Figure 3.4  Expanded view of infrared spectra of DMAAs in a) $H_2$ at 200°C, b) $H_2$ at 430°C, c) $H_2$ at 565°C, d) He at 465°C, e) $D_2$ at 500°C, and f) $D_2$ at 540°C.
Table 3.2  Assignment of major bands in infrared spectra for DMAP, DMAAAs and DMASb

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>DMAP</th>
<th>DMAAAs</th>
<th>DMASb</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1080</td>
<td>1058</td>
<td>1065</td>
<td></td>
<td>(\rho) CH(_3)</td>
</tr>
<tr>
<td>1169</td>
<td>1156</td>
<td>1163</td>
<td></td>
<td>(\rho) CH(_3)</td>
</tr>
<tr>
<td>1203</td>
<td>1195</td>
<td>1185</td>
<td></td>
<td>(\rho) CH(_3)</td>
</tr>
<tr>
<td>1280</td>
<td>1252</td>
<td>1248</td>
<td></td>
<td>(v)(_{\text{as}}) C-N-C</td>
</tr>
<tr>
<td>1460</td>
<td>1464</td>
<td>1464</td>
<td></td>
<td>(\delta) CH(_3)</td>
</tr>
</tbody>
</table>
Table 3.3  Infrared bands for pyrolysis products

<table>
<thead>
<tr>
<th>Name</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylamine</td>
<td>1462</td>
<td>δ CH₃</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td>Methylmethyleneimine</td>
<td>1661</td>
<td>ν C=N</td>
</tr>
<tr>
<td></td>
<td>1475</td>
<td>δ CH₂</td>
</tr>
<tr>
<td></td>
<td>1444</td>
<td>δ CH₃</td>
</tr>
<tr>
<td></td>
<td>1220</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td></td>
<td>1026</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td>Methyleneimine</td>
<td>1638</td>
<td>ν C=N</td>
</tr>
<tr>
<td></td>
<td>1453</td>
<td>δ CH₂</td>
</tr>
<tr>
<td></td>
<td>1342</td>
<td>δ CNH</td>
</tr>
<tr>
<td></td>
<td>1055</td>
<td>ρ CH₂</td>
</tr>
<tr>
<td>Methane</td>
<td>3016</td>
<td>ν3 CH₄</td>
</tr>
<tr>
<td></td>
<td>1306</td>
<td>ν4 CH₄</td>
</tr>
<tr>
<td>Ammonia</td>
<td>3444</td>
<td>ν3 NH₃</td>
</tr>
<tr>
<td></td>
<td>1626</td>
<td>ν4 NH₃</td>
</tr>
<tr>
<td>Phosphine</td>
<td>2323</td>
<td>ν1 PH₃</td>
</tr>
</tbody>
</table>
Methyleneimine is also detected by the appearance of peaks at 1638 cm\(^{-1}\) attributed to the C=N vibrational mode and a peak at 1453 cm\(^{-1}\) corresponding to the CH\(_2\) bending modes of the molecule.\(^{85}\) The N–H vibrational mode of the imine at 3400 cm\(^{-1}\) was again not detected because of its weak infrared adsorptivity. Methane, represented by sharp peaks at 3016 and 1306 cm\(^{-1}\), is observed as well at this temperature.\(^{73,84}\)

When the pyrolysis temperature is further increased to 565°C, new gas phase reaction products are formed as evidenced in the top spectra of Figure 3.2. Methane peak at 1306 cm\(^{-1}\) is increased. The formation of dimethylamine and methylmethyleneimine is reduced and a new weak peak at 1625 cm\(^{-1}\) emerges (see Figure 3.4). This peak is assigned to deformation stretching of NH\(_3\).\(^{73,84}\) The assignment of ammonia is supported by the simultaneous appearance in fluoride fiber experiments of another band at 3334 cm\(^{-1}\) (not shown), representing vibrational stretching of the molecule.

Figure 3.5a shows variations in characteristic peak intensities for the products as a function of temperature. IR signals were normalized with respect to their maximum value and corrected for possible absorption by unreacted parent molecules in the low temperature region adjacent to the IR windows. Absorption at 1195 cm\(^{-1}\) was used to represent the parent molecule, since none of the decomposition products had strong vibrational modes in this spectral region. Methane, methylmethyleneimine and methyleneimine are represented by bands at 1306, 1661 and 1638 cm\(^{-1}\), respectively. Dimethylamine is followed by the absorption intensity at 1155 cm\(^{-1}\) after subtraction of contributions from the parent reagent.

DMAAs decomposition was also done in He carrier gas. Dimethylamine (1155 cm\(^{-1}\)), methylmethyleneimine (1661 cm\(^{-1}\)), methyleneimine (1638 cm\(^{-1}\)) and methane (1306 cm\(^{-1}\)) were again the major products, as shown in
Figures 3.3 and 3.4. However, no absorption at 1625 cm\(^{-1}\) by NH\(_3\) was detected. This behavior would be expected since no excess hydrogen would be available for the formation of ammonia during the pyrolysis of dimethylamine.

Figure 3.5b shows the normalized intensities of the pyrolysis products in He as functions of decomposition temperature. The same IR adsorption bands as in the H\(_2\) case (Figure 3.5a) are used to represent the decomposition products. Table 3.4 summaries the relative peak intensities of the maximum product with respect to the parent molecule. Comparison of Figures 3.5a and 3.5b reveals that the decomposition temperature, corresponding to 50\% conversion, is 25\(^\circ\)C lower in H\(_2\) carrier gas than in He. In addition, from Table 3.4, concentrations of dimethylamine and methane are much less in He than those observed in H\(_2\). Dimethylamine, methylmethyleneimine and methyleneimine intensities also begin to decrease at lower temperature in H\(_2\) as compared to He. The observations suggest that hydrogen radical reactions play an important role in the gas phase decomposition mechanisms.

Reduced IR transmissivity around 2200 cm\(^{-1}\) because of Se-H absorption bands in the fiber material limits the observation of vibrational modes around 2200 cm\(^{-1}\); specifically, As-H, which would be a product from a \(\beta\)-hydrogen transfer reaction.\(^{73,84}\) To explore the potential formation of AsH, decomposition experiments were also carried out using D\(_2\).

The use of the isotope is expected to shift the As-H band out of the 2200 cm\(^{-1}\) window to AsD vibrational modes at 1523 cm\(^{-1}\). The spectra of DMAAs in D\(_2\) at 500\(^\circ\)C are shown in Figure 3.3 and an expanded view of the spectra region at 1600-1700 cm\(^{-1}\) is shown in Figure 3.4. The spectra are nearly identical to those collected in H\(_2\) and He ambients, and there is no evidence of deuterated arsine vibrational modes at 1523 cm\(^{-1}\). The CH\(_3\) bond
deformation of dimethylamine [(H₃C)₂NH] and possibly N-deuterated dimethylamine [(H₃C)₂ND] are observed at 1155 cm⁻¹. Unfortunately, the N–D and N–H bands for dimethylamine are so weak that they could not be detected by the existing experimental set-up. Methane (CH₄) absorption at 1306 cm⁻¹, methylmethyleneimine at 1661 cm⁻¹ and methyleneimine at 1638 cm⁻¹ are also observed. When the temperature is increased to 540°C, a new vibrational mode emerges at 1630 cm⁻¹, as shown in Figure 3.4. This mode is assigned to the C=N stretching of deuterated methyleneimine (H₂C=ND) as reported by Hamada.⁸⁵

CH₃D is also observed as a reaction product at high temperature. One of the differences between spectra of CH₃D and CH₄ is the appearance of a new sharp peak at 1155 cm⁻¹ due to CH₃ deformation vibrations of CH₃D.⁷³ This vibrational mode is easily distinguished compared to those of dimethylamine, which feature triplet peaks centered at 1155 cm⁻¹.⁸² The C-D stretching vibrational mode of the molecule cannot be observed in the present fiber set-up since the adsorption band is located in the cut-off region of the chalcogenide fiber, ~2200 cm⁻¹.

The N-D vibrational modes of deuterated amine species (NHₓD₃₋ₓ) is not observed in the spectra at high temperature, which may be rationalized in terms of the combination of a weak infrared cross section, a low concentration of the species. By comparison, the intensity of the NH₃ signal detected for pyrolysis in H₂, using the equivalent vibrational mode at 1625 cm⁻¹, is very weak and close to the minimum detection limit.
Figure 3.5  Decomposition products of DMAAs in a) H₂, and b) He. Δ = Parent molecule, O = dimethylamine, + = methane, X = methyleneimine, ◊ = methyl-methyleneimine. Table 3.4 lists the ratio of maximum intensity of the products with respect to that for the parent molecules.
Table 3.4  The Comparison of relative peaks for decomposition products and parents in H₂ and He

<table>
<thead>
<tr>
<th>Compound</th>
<th>Products</th>
<th>In H₂</th>
<th>In He</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMAAs</td>
<td>Parent</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Dimethylamine</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Methyl-methyleneimine</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Methyleneimine</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Methane</td>
<td>1.15</td>
<td>0.30</td>
</tr>
<tr>
<td>DMAP</td>
<td>Parent</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Dimethylamine</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Methyl-methyleneimine</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Methyleneimine</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Methane</td>
<td>0.76</td>
<td>0.22</td>
</tr>
<tr>
<td>DMASb</td>
<td>Parent</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Dimethylamine</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Methyl-methyleneimine</td>
<td>0.12</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Methyleneimine</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Methane</td>
<td>0.76</td>
<td>0.19</td>
</tr>
</tbody>
</table>
3.3.2 Decomposition of DMAP

Molecular beam mass spectra of DMAP in 30 Torr of H₂ at cell temperatures of 50°C and 450°C are shown in Figure 3.6. The fragmentation pattern of DMAP has been reported in the literature and a summary of the peak assignments is given in Table 3.1. At 450°C, the intensity of the peaks from the parent molecules (m/e = 60, 76, 120 and 163) are reduced significantly reflecting decomposition of the parent molecule. The major reaction products are, as in the case of DMAAs, methylmethylenemime and dimethylamine with characteristic signals at m/e = 42 and m/e = 44, respectively. P₂ (m/e = 62) and P₄ (m/e = 124) are also observed, but no evidence of organophosphine intermediates is found.

As in the case of DMAAs, the gas-phase pyrolysis of DMAP was investigated by FTIR at 600 Torr in H₂, D₂, and He ambients. The spectra for decomposition of DMAP in H₂ are shown in Figure 3.8. The peak assignment for the DMAP molecule follows that of DMAAs and is given in Table 3.2. The spectra recorded at 500°C show a decrease in the relative intensities of the bands at 1204 cm⁻¹ and 1155 cm⁻¹ as a result of the decomposition of the parents (1204 cm⁻¹) and the formation of dimethylamine (1155 cm⁻¹). Methane with the sharp bands at 1306 and 3016 cm⁻¹ is observed. The presence of the product methylmethylenemime is also apparent by absorptions at 1661, 1444 and 1475 cm⁻¹. An expanded view of the spectral region 1600-1700 cm⁻¹, (Figure 3.9) reveals the presence of the C=N vibration mode of methyleneimine at 1638 cm⁻¹. Further increasing the temperature to 630°C, leads to the formation of more methane and a new peak at 1625 cm⁻¹ corresponding to NH₃.
Figure 3.6  Molecular beam mass spectra of DMAP at a) 50°C, and b) 450°C.
Figure 3.7  Infra-red spectra of DMAP in H₂ at a) 360°F, b) 500°F, and c) 630°F. Spectra b is after subtracting the parents contribution.
Figure 3.8  Expanded view of infrared spectra of DMAP in a) H$_2$ at 500°C, b) H$_2$ at 630°C, c) He at 515°C, d) D$_2$ at 505°C, e) D$_2$ at 565°C, and f) He at 560°C.
Figure 3.9  Decomposition products of DMAP in a) H₂, and b) He. Δ = parent molecule, O = dimethylamine, + = methane, X = methyleneimine, ◊ = methyl-methyleneimine. Table 3.4 listed the ratio of maximum intensity of the products with respect to that for the parent molecules.
At temperatures exceeding 500°C, a new absorption band, centered at 2322 cm\(^{-1}\) is observed (Figure 3.7). The peak position and the shape resemble that of the PH\(_3\) molecule vibrational mode.\(^{73}\) The signal is stronger than that for NH\(_3\) because the observed vibrational mode of PH\(_3\) at 2322 cm\(^{-1}\) has approximately a 6 times larger infrared cross-section.\(^{86}\) In D\(_2\) ambient (Figures 3.9 and 3.10), the peak position remains the same, but the peak shape is different and considerably weakened. Moreover, a new band appears at 1685 cm\(^{-1}\) that is not observed for decomposition in H\(_2\) and He. This spectral position is very close to that reported for P–D vibrational bands of PH\(_2\)D,\(^{87}\) indicating the formation of PD\(_x\)H\(_{3-x}\) (\(x = 1\) or 2) during pyrolysis in D\(_2\). Deuterated methyleneimine (H\(_2\)C=ND) and CH\(_3\)D are again observed as products of the gas phase reactions.

Figures 3.9(a) and (b) show the decomposition products in H\(_2\) and He, respectively, as a function of the gas-phase temperature. The reagent and products are characterized by vibrational modes equivalent to those used in the case of DMAAs. In both gases, dimethylamine, methylmethyleneimine, methyleneimine and methane appear as soon as the reactant starts to decompose. Decomposition in He leads to the formation of less dimethylamine and methane. No evidence for the formation of PH\(_3\) is observed for gas-phase decomposition of DMAP in He.

### 3.3.3 Decomposition of DMASb

Decomposition studies of DMASb were carried out solely in the FTIR-fiber set-up. Spectra of DMASb in H\(_2\) at 200°C, 360°C and 630°C are shown in Figure 3.10. The 200°C spectrum represents DMASb before decomposition. Peak assignments are given in Table 3.2 and they are equivalent to those for
DMAAs and DMAP. When the temperature is increased to 360°C, DMASb decomposes, partially producing methylmethyleneimine (1661, 1444 and 1475 cm\(^{-1}\)), dimethylamine (1155 and 1460 cm\(^{-1}\)) and methane (1306, 3016 cm\(^{-1}\)) analogous to the pyrolysis of DMAAs and DMAP. At 630°C, the concentrations of dimethylamine and methylmethyleneimine are reduced with additional formation of methane and ammonia. In D\(_2\), deuterated methyleneimine (1630 cm\(^{-1}\)) and CH\(_3\)D are again detected as in the pyrolysis of the other \textit{tris}-dimethylamino sources.

Normalized variations in reagents and product concentrations with temperature are summarized in Figure 3.11. In H\(_2\), dimethylamine and methylmethyleneimine are produced as the reagent starts to decompose. Methane and methyleneimine start to pickup production at around 400°C and ammonia is generated at temperature above 550°C. The study of gas-phase pyrolysis in He shows that the start of decomposition occurs \(~25°C higher than in H\(_2\). There is less production of methane and dimethylamine, and no formation of ammonia similar to those observed in DMAAs and DMAP.
Figure 3.10  Infrared spectra of DMASb in H$_2$ at a) 200°C, b) 360°C, and c) 630°C. Spectra b is after subtracting the parents contribution.
Figure 3.11 Decomposition products of DMASb in a) H₂, and b) He. Δ = parent molecule, O = dimethylamine, + = methane, X = methyleneimine, ○ = methyl-methyleneimine. Table 4 lists the ratio of maximum intensity of the products with respect to that for the parent molecules.
3.4 Discussions

3.4.1 Gas-phase pyrolysis pathways of tris-dimethylamino group V reagents

The decomposition mechanism, shown schematically in Figure 3.13, is consistent with the experimental data. The relative widths of the reaction arrows from the tris-dimethylamino reagent are used to indicate the importance of the reaction. The gas-phase decomposition of the molecules is initiated and dominated by the homolysis reaction:

\[(\text{CH}_3)_2\text{N})_3\text{E} \rightarrow (\text{CH}_3)_2\text{N})_2\text{E} + (\text{CH}_3)_2\text{N}^*\]  

(3.1)

where E represents P, As, or Sb. A comparison between the degree of decomposition of DMAAs, DMAP and DMASb as a function of temperature, is given in Figure 3.12. With increasing temperature, DMASb decomposes first, followed by DMAAs, and at higher temperatures, DMAP. This trend in decomposition temperature is consistent with the bond strength of N–E being weakest for E = Sb and strongest for E = P.

The continuous curves in the graph represent the fitted model based on an analysis of a first-order decomposition reaction in a well-mixed reactor. The corresponding activation energies are summarized in Table 3.5. The same preexponential factor of $10^{-13} \text{ (s}^{-1})$ was assumed for all three pyrolysis reactions since the fit to data did not provide statistically significant differences between the individual preexponential factors. The value of $10^{-13} \text{ (s}^{-1})$ is consistent with simple transition state considerations. The activation energy for pyrolysis of DMAP is very close to the reported P–N bond energy of 55 kcal/mole\(^57\), which indicates that the rate limiting step in the gas-phase decomposition is the homolysis of the N–P bond.
Table 3.5. First-Order Kinetic Rate Parameters for the *tris*-dimethylamino Reagents

<table>
<thead>
<tr>
<th></th>
<th>DMAP</th>
<th>DMAS</th>
<th>DMASb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (Kcal/mol)</td>
<td>50.6</td>
<td>44.0</td>
<td>41.1</td>
</tr>
</tbody>
</table>
Figure 3.12  Comparison of decomposition profiles for DMAP, DMAAs and DMASb. Points represent experimental data; curves are computed on the basis of first-order kinetics (cf. Table 4.4).
Figure 3.13  Schematic of gas-phase decomposition pathways for [(CH₃)₂N]₃E, E = P, As, and Sb.
For each reagent, decomposition commences at lower temperatures in H₂ than in He. Moreover, the amounts of dimethylamine and methane generated in a H₂ ambient are larger than those observed in He carrier gas. These observations suggest involvement of hydrogen radicals in a secondary decomposition path (see Figure 3.13). In the presence of H₂, the dimethylaminyl radical, formed in the homolysis reaction (1), abstracts H and produces a hydrogen radical:

\[(\text{CH}_3)_2\text{N•} + \text{H}_2 \rightarrow (\text{CH}_3)_2\text{NH} + \text{H•}\]  \hspace{1cm} (3.2)

The H• radical can then further accelerate the decomposition of the amino reagent according to reactions of the form:

\[(\text{CH}_3)_2\text{N}_x\text{E} + \text{H•} \rightarrow (\text{CH}_3)_2\text{N}_{x-1}\text{E} + (\text{CH}_3)_2\text{NH}, \ x = 1,2,3 \]  \hspace{1cm} (3.3a)

\[(\text{CH}_3)_2\text{N}_x\text{E} + \text{H•} \rightarrow (\text{CH}_3)_2\text{N}_{x-1}\text{E} + \text{H}_2 + \text{H}_2\text{C=NCCH}_3, \ x = 1,2,3 \]  \hspace{1cm} (3.3b)

Analogous reactions take place in D₂ with the formation of deuterium radicals and subsequent attack on the amino reagent.

Dimethylaminyl radicals can also themselves accelerate decomposition of the molecule via the reaction:

\[(\text{CH}_3)_2\text{N}_x\text{E} + (\text{CH}_3)_2\text{N•} \rightarrow (\text{CH}_3)_2\text{N}_{x-1}\text{E} + (\text{CH}_3)_2\text{NH} + \text{H}_2\text{C=NCCH}_3 \]  \hspace{1cm} (3.4)

The participation of H• in the pyrolysis through reactions (3.2) and (3.3a) is apparent in the increased amount of dimethylamine relative to methylmethylenimine in H₂ as compared to He. The effect is particularly noticeable for pyrolysis of DMAAs, where ~1.5 times more dimethylamine is produced than in He.

The other possible channel for production of dimethylamine and methylmethylenimine in both H₂ and He is the disproportional reaction:

\[(\text{CH}_3)_2\text{N•} + (\text{CH}_3)_2\text{N•} \rightarrow (\text{CH}_3)_2\text{NH} + \text{H}_2\text{C=NCCH}_3 \]  \hspace{1cm} (3.5a)

This pathway is important in reactions involving dimethylaminyl radicals
generated in photolysis and pyrolysis of nitrogen containing compounds such as tetramethyl-2-tetrazene, trimethylamine, dimethylamine and tetramethylhydrazine\textsuperscript{88, 89}.

A potential competing step to reaction (3.5a) is the recombination of two dimethylaminyl radicals to produce tetramethylhydrazine (TMH):

\[ (\text{CH}_3)_2\text{N}\bullet + (\text{CH}_3)_2\text{N}\bullet \rightarrow (\text{CH}_3)_2\text{N-N(CH}_3)_2 \] \hspace{1cm} (3.5b)

No TMH was detected as the products of decomposition of trimethylamino compounds in He, H\textsubscript{2} or D\textsubscript{2}. Using the very low pressure pyrolysis technique, Lazarou and Papagiannakopoulos\textsuperscript{90} determined the rate constant for reactions (3.5a) and (3.5b) to be:

\[ k_{5a} = (4.10\pm 0.52) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

and

\[ k_{5b} = (1.70\pm 0.19) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \]

respectively, at room temperature. Since the reactions have no activation barrier, the rate constant data predict the reaction (3.5a) to be more than twice as fast as the recombination reaction (3.5b). Simulation of pyrolysis of TMH for the present experimental conditions with the use of reported kinetic data\textsuperscript{91,92} reveals that TMH decomposes at temperatures similar to those required to pyrolyse the organometallic reagents. Thus, it is unlikely that TMH will be a stable pyrolysis product.

Additional reactions of the dimethylaminyl radical include a recombination reaction with hydrogen radicals to produce dimethylamine, or a hydrogen abstraction reaction to produce methylmethylenimine, as observed in the very low pressure pyrolysis of methylhydrazine:\textsuperscript{92}

\[ (\text{CH}_3)_2\text{N}\bullet + \text{H}\bullet \rightarrow (\text{CH}_3)_2\text{NH} \] \hspace{1cm} (3.6)

\[ (\text{CH}_3)_2\text{N}\bullet \rightarrow \text{H}_2\text{C=NCH}_3 + \text{H}\bullet \] \hspace{1cm} (3.7)

\[ (\text{CH}_3)_2\text{N}\bullet + \text{RH} \rightarrow (\text{CH}_3)_2\text{NH} + \text{R}\bullet \] \hspace{1cm} (3.8)
where H is any organic H-donor molecules.

At temperatures higher than 400°C, the dimethylaminyl radical decomposes to form a methyl radical and methyleneimine \(^{89}\) according to:

\[
(\text{CH}_3)_2 \text{N} \cdot \rightarrow \text{CH}_3 \cdot + \text{H}_2\text{C}=\text{NH}
\]  

(3.9)

This reaction is responsible for the formation of methyleneimine in decomposition under He. N-deuterated methyleneimine (H\(_2\)C=ND), which is observed in D\(_2\) ambients, is likely generated in a radical exchange reaction of D with methylmethyleneimine:

\[
\text{H}_2\text{C}=\text{NCH}_3 + \text{D} \cdot \rightarrow \text{H}_2\text{C}=\text{ND} + \text{CH}_3 \cdot
\]

(3.10)

This reaction does not take place in He. As a consequence, the formation of methylmethyleneimine is observed up to 550°C in He in contrast to H\(_2\) and D\(_2\) cases where the methylmethyleneimine concentration begins to decrease at temperatures as low as 425°C.

The methyl radical formed in reaction (3.9) and (3.10) participates in abstraction and recombination reactions to yield methane:

\[
\text{CH}_3 \cdot + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} \cdot
\]

(3.11)

\[
\text{CH}_3 \cdot + \text{H} \cdot + \text{M} \rightarrow \text{CH}_4 + \text{M}
\]

(3.12)

\[
\text{CH}_3 \cdot + \text{RH} \rightarrow \text{CH}_4 + \text{R} \cdot
\]

(3.13)

\[
\text{CH}_3 \cdot + (\text{CH}_3)_2 \text{N} \cdot \rightarrow \text{CH}_4 + \text{H}_2\text{C}=\text{NCH}_3
\]

(3.14)

Reactions (3.11) and (3.12) are primarily responsible for the formation of methane in H\(_2\), whereas reactions (3.13) and (3.14) are the primary sources of methane in He.

The recombination reaction:

\[
\text{CH}_3 \cdot + (\text{CH}_3)_2 \text{N} \cdot \rightarrow (\text{CH}_3)_3 \text{N}
\]

(3.15)

to form trimethylamine could potentially compete with reaction (3.14), but no trimethylamine reaction is observed as a reaction product in the decomposition. At the elevated temperatures, it is very likely that the
recombination reaction (3.15) proceeds at a slower rate than the disproportionation reaction (3.14), similar to the case of reactions of (3.5b) and (3.5a) for the dimethylaminyl radicals. Trimethylamine is reported to decompose to methane and methylmethyleneimine through a first order process with $10^{14.3}e^{-\frac{29.5}{T}}(s^{-1})$. Simulations of decomposition in the present gas cell shows trimethylamine to decompose completely in the temperature range 500-600°C. It is therefore not expected to be a major product of the pyrolysis product.

At temperatures exceeding 550°C, homolysis of the N-C bond commences, as evidenced by decreases in concentrations of methylmethyleneimine, methyleneimine and dimethylamine, along with the continual increase in the production of ammonia at elevated temperatures. This process is probably initiated by the pyrolysis of dimethylamine and dimethylaminyl radicals. The decomposition of dimethylamine has been reported to follow first-order kinetics with activation energy of 46.6 kcal and pre-exponential factor of $10^{10.5} s^{-1}$. Simulation of the degree of decomposition of dimethylamine under the current gas cell conditions shows that the compound starts to decompose at temperatures as low as 550°C.

The breaking of the C–N bond at elevated temperatures is a likely explanation for the observed nitrogen incorporation in AlGaAs. Alternatively, the nitrogen incorporation may be attributed to strong interactions of the tris-dimethylamino reagents with group III alkyls. In any case, the onset of decomposition of the dimethylamine group marks the upper limit for gas-phase temperatures suitable for growth of high-quality III-V compound semiconductors with the new tris-dimethylamino reagents.
3.4.2 Surface effects

The possible role of reactor surfaces in the decomposition reactions was explored by DMAAs by introducing large surface areas of SiO$_2$ and GaAs, as described in the Experimental Section. The degree of pyrolysis of DMAAs was affected by the presence of a high surface area of packing materials (see Figure 3.14). In the presence of a high surface area of SiO$_2$, the decomposition temperature is lowered only by 25°C and the product distribution is similar to that observed for the "empty" cell. These observations suggest that the decomposition reactions observed in the original gas cell proceed through homogeneous pathways.

Heterogeneous reactions are clearly involved when the cell is packed with GaAs chips. Decomposition starts at 250°C, about 100°C lower than the results presented above for the empty gas cell. The first major reaction product to appear with increasing decomposition temperature is dimethylamine, followed by methylmethyleneimine about 50°C above the initial decomposition temperature. The DMAAs pyrolysis behavior over a GaAs surface is in agreement with results of temperature programmed desorption (TPD) studies of DMAAs on GaAs, which show that the primary channel for DMAAs is surface reactions involving the generation of dimethylamine radicals.$^{61}$ The presence of H$_2$ again accelerates the decomposition relative to the He case by the gas-phase formation of H•, which subsequently attacks the parent molecule [cf. reactions (3.2) and (3.3)]. Methylmethyleneimine is most likely produced in gas-phase reactions [e.g., reaction (3.4)], but some methylmethyleneimine could also result from a β-hydrogen transfer surface reaction pathway reported in TPD investigations.$^{61}$
Figure 3.14  Decomposition of DMAAs in the presence of a high surface area of: SiO$_2$ (O) in H$_2$; GaAs in H$_2$(Δ); GaAs in He (+). (X) is decomposition with no packing material.
3.5 Conclusions

Pyrolysis studies of tris-dimethylamino-phosphine-arsine and stibine precursors for OMCVD of InP, GaAs, InSb and related compounds, show that the reagents primarily decompose through homolysis of the central atom (P, A, Sb)-dimethylamine bond. The decomposition occurs at relatively lower temperatures than the tri-alkyl sources. Moreover, the corresponding group V species is formed without detectable side reactions to other organogroup V reactions. These characteristics make the tris-amino reagents suitable candidates for synthesis of III-V compound semiconductors, provided the gas-phase temperature above the growth surface is low enough (≤500°C) to avoid decomposition of the dimethylaminyl radical and related species. The large number of lone pair orbitals on the amino groups, as well as the central group V atom, however, raise the possibility of strong Lewis acid base interactions leading to the formation of adducts with group III alkyls. Such interactions could potentially result in reduced growth performance.
Chapter 4:

Gas Phase Interactions Between Tris-Dimethylamino Group V Compounds with Trialkyl Group III sources

4.1 Introduction

Tris-dimethylamino-arsine (DMAAs), -phosphine (DMAP) and -stibine (DMASb) represent a new group of organometallic group V compounds for OMCVD, in which the group V element is bonded directly to three nitrogen atoms of the dimethylamino ligands.\textsuperscript{56} The low decomposition temperatures of these compounds are attractive for OMCVD, e.g. for low temperature growth of Sb containing materials, used for infrared applications.

The use of DMAP, DMAAs and DMASb for OMCVD has been demonstrated for epitaxial growth of GaAs, InAs, InP and InSb films.\textsuperscript{58, 63, 94} However, growth of aluminum containing III-V compound semiconductor films using DMAAs has been unsuccessful. Growth using DMAAs, TMAI, TMG or TMIn produced AlGaAs\textsuperscript{58, 94} and AlInAs\textsuperscript{94} films respectively with a rough morphology. Moreover, SIMS measurements showed significant carbon and nitrogen incorporation in the films.\textsuperscript{58}

Strong gas phase interactions between the empty bonding orbital of the Al atom and the lone pair electrons of N in the dimethylamino ligands has been proposed as a reason for the unsuccessful OMCVD growth.\textsuperscript{58} The gas phase pyrolysis study in Chapter 3 showed that the dimethylamino compounds decompose at relatively low temperature. At temperatures higher than 550°C,
decomposition of the dimethylaminy1 radical may lead to incorporation of nitrogen and carbon fragments.

Group III trialkyl precursors and dimethylamino ligands interact at room temperature through Lewis acid-base reactions involving the lone pair electrons on the group V atom, specifically N, and the coordinationally unsaturated group III atom. Such interactions have been observed at room temperature during OMCVD of GaN using ammonia and TMG, leading to the formation of black polymeric deposits near the entrance of the mixing zone. The basicity of the dimethylamine molecule is stronger than that of ammonia and, therefore, the tris-dimethylamino compounds would be expected to show a high affinity to form adducts.

4.2 Motivation

Evidence for the formation of adducts was apparent in GaSb growth experiments with triethylgallium (TEG) and DMASb at 150 torr. Formation of a clear liquid condensate was observed in the mixing zone of reactor entrance. The condensate turned into white powder upon exposure to air. Moreover, the growth process suffered from irreproducible film morphology. The surface, which was continuously monitored by laser scattering technique, was specular during the growth. However, as soon as the supply of organometallic to the reactor was turned off at the end of the growth, it turned hazy and rough (Figure 4.1). Auger electron spectroscopy analysis determined that the growth defect was caused by the presence of excess Sb species on the surface. These observations suggest that a strong interaction between DMASb and TEG produce a liquid "adduct" in the mixing zone, which may reevaporate back to the growth region at the end of the run resulting in degradation of surface
morphology. This phenomenon is similar to the parasitic effect observed during
the growth of AlSb films using TTBAI and TESb (Section 2.5.2).

The mechanism underlying this parasitic process is not fully understood.
In this chapter, room temperature reactions between the group III and V
reagents are explored in order to probe the mechanism of interactions of tris-
dimethylamino compounds with conventional group III precursors in a novel in-
situ FTIR system. This set up is used to monitor gas phase products resulting
from mixing of the precursors. Ex-situ NMR spectroscopy is also employed to
analyze both gas phase and liquid phase products.

4.3 Experimental set-up and procedures

4.3.1 In-situ FTIR spectroscopy

The in-situ FTIR experiments were performed by using a conventional
OMCVD precursor delivery system shown in Figure 4.2. The spectroscopy set-
up consisted of a 12.7 cm gas cell constructed from a quartz tube (2.5 cm
diameter), with quartz flanges fused to the tube ends (cf. Figure 4.2). KBr
windows with viton o-ring seals were placed at each end and sealed with
stainless steel flanges. Two 0.635 cm OD quartz tubes, fused to the body of the
cell, served as the separate inlet ports for the group III and V organometallic
sources. The gas exited the cell through an outlet port located adjacent to one of
the IR window. Each port was equipped with a valve. The cell could be heated
to 650°C with a resistive heater attached to the wall of the gas cell. The
temperature was determined by inserting a type-K thermocouple into a
thermocouple well penetrating into the gas-cell.
Figure 4.1  Surface morphology of GaSb film grown using DMASb and TEG.
The FTIR spectrometer was a KVB Analect Diamond-20 equipped with a DTGS detector and controlled by a Dell 486-50 MHz computer. The gas cell was placed inside the sample compartment of the spectrometer and a single IR transmission through the gas cell was used.

For each mixing experiment, the gas cell was evacuated and the carrier gas flows through the organometallic bubblers were established and directed to the vent line. The outlet valve to the gas cell was then closed, and a background spectrum was collected. Both the group III and group V flows were switched-in simultaneously to the gas cell. Once the pressure of the gas cell reached 600 torr, the inlet valves were closed and an infrared spectrum of the mixture was taken every minute to monitor changes in the gas phase composition. The organometallic partial pressure in the gas cell was in the range of 0 to 4 torr. An average of 128 scans and 4 cm\(^{-1}\) resolution were used when collecting the spectra.

4.3.2 Nuclear magnetic resonance experiments

In the ex-situ NMR experiments, sample collection was carried out in a reactor vessel constructed of Pyrex glass shown in the inset of Figure 4.2. The vessel consisted of two collection cells. The first cell, which had two inlets and one outlet, collected room temperature condensate. The second cell trapped volatile by-products of the reactions in the first cell. This cell was kept at liquid nitrogen temperature during the mixing experiment.

Sample collections were performed by using the same source delivery system as in the FTIR experiments. The NMR vessel replaced the IR gas cell. Once the hydrogen flow to the organometallic bubblers was stabilized, the organometallic flows were switched to the vessel and the pressure was increased
to 600 torr. A total flow of 100 sccm was used in these runs to allow complete mixing. Organometallic flow rates between 10 to 15 μmol/min. were used. The flow was terminated after approximately a 50 mg sample was collected in each cell.

The cell was then isolated by closing all the valves, detached from the gas handling system, and then transferred to a nitrogen glove box. In the glove box, each sample was dissolved in 500 mg of 99.6% d₆-benzene (Cambridge Isotope) and then transferred to an NMR tube. Carbon-13 and proton NMR spectra were collected using a Varian XL-300 NMR spectrometer.

Organometallic sources. DMAP, DMAAs and DMASb, TMIn (Air Products and Chemicals), TMG, TMAI and TEG (Texas Alkyls) were electronic grade and supplied in stainless steel bubblers. H₂ (Matheson, 99.9995%) was used as the carrier gas for the experiments.
Figure 4.2  Experimental system for *in-situ* FTIR and *ex-situ* NMR studies. The figure in the box shows the set-up for collecting NMR samples.
4.4 Results

4.4.1 Reactions of DMAP with trialkyl group III reagents

Interactions between pairs of group III alkyls and group V dimethylamino sources are first studied by the in-situ FTIR technique. Figure 4.3 shows the gas phase spectra of a) TMAI, b) DMAP and c) a mixture of TMAI and DMAP. The spectrum of the mixture is collected immediately after the gas cell pressure reaches 600 torr. The spectrum of the mixture differs from the sum of the DMAP and TMAI. It is instead assigned to the adduct shown schematically in Figure 4.5a.

Tables 4.1 and 4.2 show the peak assignment for the trialkyl sources and the adduct with DMAP. The break up of the TMAI dimer into a monomer in the adduct results in the lost of \( \rho \text{CH}_3 \) of TMAI peaks at 770 cm\(^{-1} \) and the shift of \( \nu\text{Al-C} \) from 565 cm\(^{-1} \) to 620 cm\(^{-1} \). A new peak at 508 cm\(^{-1} \) is assigned to the adduct bond between Al and N.\(^{96} \) Upon adduct formation, the DMAP peak at 1270 cm\(^{-1} \) \(^{81} \nu \text{C-N-C} \) becomes broader and the maximum is shifted to 1280 cm\(^{-1} \); the peak at 1160 cm\(^{-1} \) (\( \rho \text{CH}_3 \) of DMAP) is decreased. The peak of \( \nu \text{P-N-C} \) shifts to 965 cm\(^{-1} \) from 959 cm\(^{-1} \).

The observed vibrational bands for the mixture are similar to those registered for bis-dimethylaminomonochlorophosphorous (P(N(CH\(_3\))\(_2\)Cl)\(^{81} \) (See Table 4.2). There is a particularly strong resemblance in the location of vibrational modes correspond to \( \nu \text{C-N-C} \) (1280 cm\(^{-1} \)), \( \nu \text{P-N-C} \) (965 cm\(^{-1} \)) and \( \nu \text{P-N} \) (710 and 674 cm\(^{-1} \)) suggesting that the adduct contains two identical dimethylamino groups analogous to those in P(N(CH\(_3\))\(_2\)Cl. Furthermore, for the adduct, the number of \( \nu \text{P-N} \) peaks increase from two in DMAP (at 674 and 649 cm\(^{-1} \)) to three peaks at 709, 690 and 660 cm\(^{-1} \). One mode is assigned to the P-
N bond where N is bonded to Al. The other two modes are the symmetrical and unsymmetrical stretching vibrations of the P-N bonds to the free dimethylamino groups.

The FTIR observations are consistent with DMAP and TMAI forming an adduct by Lewis acid-base interactions between one of the N atoms in DMAP and the Al atom as illustrated in Figure 4.5a. To further explore the nature of the interaction, in-situ FTIR experiments were carried out for different molar ratios of the starting group III and V sources. Varying the molar ratio of the incoming organometallic sources did not produce any changes in the spectrum of the adduct. The amount of excess organometallic reagents was quantified and compared to the amount of both organometallic sources fed into the gas cell. The results showed that one mole of TMAI was consumed for every mole of DMAP in support of the IR assignment of the adduct structure shown in Figure 4.5a.

The NMR results further suggest the adduct structure. Gas phase reactions of DMAP and TMAI at room temperature immediately produce a solid white deposit on the wall of the NMR mixing tube. This compound dissolves readily in d$_6$-benzene. Proton NMR spectrum of the deposit shows three peaks at 2.203 and 2.304 and -0.290 ppm. The first two peaks are assigned to the proton from dimethylamino groups, which are shifted to a lower field from the DMAP peaks at 2.425 ppm.$^{58}$ The -0.290 ppm peak is assigned to the methyl group of TMAI, which is shifted from - 0.358 ppm. The $^{13}$C NMR also shows formations of three peaks; two in the amine region at 37.01 and 36.88 ppm (DMAP at 37.9 ppm$^{58}$) and one in the aluminum alkyl region at -6.719 ppm.

The splitting and position of the $^1$H and $^{13}$C dipoles suggest that the Lewis acid base interaction between DMAP and TMAI occurs by sharing of a pair of electrons between one nitrogen atom in DMAP and the aluminum atom
in agreement with the IR results. This interaction (Figure 4.5a) breaks the symmetry of the DMAP molecule resulting in the generation of two non-equivalent dimethylamino groups; one is attached to aluminum and the other two, which are identical, remain free. As a result, the proton and $^{13}$C NMR peaks are split corresponding to the two groups of dimethylamino molecules. The interaction between aluminum and nitrogen reduces the electronegativity of the nitrogen which shifts the proton peak of dimethylamino to a lower field strength. The methyl groups attached to aluminum experience an increase in electronegativity and this results in upward shift of the proton peaks. Krannich et al. reports a similar peak shift which is observed in low temperature mono Al-N bonded adducts between DMAAs and TMAI.\textsuperscript{97}

Room temperature reactions of DMAP with TMG, TEG and TMIn produced similar adduct structure (Figure 4.5a). The infrared spectra of the adducts of a) DMAP and TMG, b) DMAP and TMIn and c) DMAP and TEG displayed in Figure 4.4 (see also Table 4.2) show similar features to the structure for DMAP + TMAI adduct, especially the dimethylamino peaks at 1460, 1280, 1190, 1160, 1064, 960 and the triplet P-N peaks at 650-700 cm$^{-1}$. Differences among the spectra in the region around 500-750 cm$^{-1}$ are caused by the contributions of $\rho_{\text{M-alkyl}}$, $\nu_{\text{M-C}}$, and $\nu_{\text{M-N}}$ ($\text{M} = \text{In, Ga}$). The TEG+DMAP spectrum shows some additional peaks at 1374 and 1401 cm$^{-1}$ from the $\delta_{\text{CH}_2}$ of the ethyl group attached to the gallium atom.\textsuperscript{96}
Figure 4.3 Infrared spectra of a) TMA, b) DMAP, c) TMA + DMAP.
Figure 4.4 Infrared spectra of a) TMG + DMAP, b) TMIn+DMAP, c) TEG+DMAP.
Figure 4.5  Proposed adduct formation pathways for trialkyl group III sources with a) DMAP, b) DMAAs.
Table 4.1. Infrared bands of trialkyl group III sources

<table>
<thead>
<tr>
<th>TMA*</th>
<th>TMG</th>
<th>TMI</th>
<th>TEG</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1470, 1419, 1380</td>
<td>δ CH₃, δ CH₂</td>
</tr>
<tr>
<td>1255ᵇ, 1211ᵗ</td>
<td>1208</td>
<td>1202</td>
<td>1208**</td>
<td>δ M-CH₃</td>
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<tr>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>768ᵇ, 697ᵗ, 608ᵇ</td>
<td>773, 725</td>
<td>730, 698</td>
<td>664**</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td>564,</td>
<td>583, 572</td>
<td>510, 497</td>
<td>547</td>
<td>ν Ga-C</td>
</tr>
</tbody>
</table>

* TMA in dimer form.
** In the assignment replace CH₃ to CH₂
  b -bridge , t - terminal
Table 4.2. Adduct between DMAP and group III sources

<table>
<thead>
<tr>
<th>DMAP + TMA</th>
<th>DMAP + TMG</th>
<th>DMAP + TEG</th>
<th>DMAP + TMI</th>
<th>P(N(CH₃)₂)₂ Cl**</th>
<th>DMAP</th>
<th>Assignment **</th>
</tr>
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<tr>
<td>1458</td>
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<td>1280</td>
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<td>1190</td>
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<td>-</td>
<td>704</td>
<td>-</td>
<td>-</td>
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<td>505</td>
<td>463</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>ν M-N</td>
</tr>
</tbody>
</table>

* ρ Al-CH₃ and ρ In-CH₃ are contained at 680-700 cm⁻¹
** From reference 81.
4.4.2 Reactions of DMAAs with trimethyl group III sources.

The gas-phase reaction of DMAAs with TMAI in hydrogen immediately produced a clear liquid, a white crystal precipitate and vapor phase products. Unlike the reactions with DMAP, the products of the mixing process strongly depend on the molar ratio of DMAAs and TMAI fed into the gas cell. Figure 4.6 compares the vapor phase products in the 2:1 of TMAI monomer to DMAAs (4.6c), the vapor phase products of the reactions in 3:1 mixture of TMAI monomer to DMAAs (4.6b) and the infrared spectra of DMAAs (4.6a). The 4.6b spectrum is obtained after subtracting excess TMAI from the mixture, spectrum 4.6a is the result of subtraction of excess DMAAs from the mixture.

The spectrum in case 4.6b (III/V = 3:1) appears to be significantly different than the reactants, i.e. TMAI (c.f. Figure 4.3a) and DMAAs (4.6a). The spectrum 4.6b matches well the published spectra of dimethyldimethylaminoaluminum dimer (Al(N(CH$_3$)$_2$)(CH$_3$)$_2$)$_2$ $^{98}$ (Table 4.3). In the case of the 2:1 mixture (Figure 4.6c), dimethyldimethylaminoarsenic (As(N(CH$_3$)$_2$)(CH$_3$)$_2$) is the other product observed along with the aluminum dimer compound.

As(N(CH$_3$)$_2$)(CH$_3$)$_2$ is the only arsenic containing species that is observed as a product of the reaction. The arsenic compound features a peak at 832 cm$^{-1}$ which is very close to the $\rho_{\text{As-CH}_3}$ in As(CH$_3$)$_y$X$_{3-y}$ (where $X$ = Cl, Br or I and $y$=1,2).$^{99}$ This peak is observed only in the reported spectrum of As(N(CH$_3$)$_2$)(CH$_3$)$_2$ but not in the IR spectrum of As(N(CH$_3$)$_2$)$_2$(CH$_3$).$^{100}$ Other characteristic peaks of As(N(CH$_3$)$_2$)(CH$_3$)$_2$ are in the region of 560-580 cm$^{-1}$, corresponding to $\nu_{\text{As-N}}$ (565 cm$^{-1}$) and $\nu_{\text{As-C}}$ (571 cm$^{-1}$).

NMR analysis of the vapor phase product for the 2:1 mixture agrees well with the infrared data. The [Al(N(CH$_3$)$_2$)(CH$_3$)$_2$]$_2$ is observed by appearance of
proton peaks at 2.060 from the dimethylamino group and at -0.59 ppm from methyl (Figure 4.7a).\textsuperscript{101} $^{13}$C data (Figure 4.7b) show a peak at + 41.5 ppm attributed to dimethylamine and at -11.56 ppm from methyl groups in agreement with the reported value.\textsuperscript{97, 101} The appearance of As(N(CH$_3$)$_2$)(CH$_3$)$_2$ is confirmed by a proton peak at + 2.42 ppm and a $^{13}$C peak at 41.95 ppm from the dimethylamino group; and a proton peak at 0.80 ppm and a $^{13}$C peak at 9.99 ppm due to the two methyl groups.\textsuperscript{97, 102} No other significant product is observed except those of excess DMAAs (a proton peak at 2.59 ppm and a $^{13}$C peak at 39.72 ppm). The proton NMR spectra of the precipitate indicate adducts containing at least three different aluminum methyls, one type of arsenic methyl and two different aluminum dimethylamino peaks. In the 3:1 mixture, only [Al(N(CH$_3$)$_2$)(CH$_3$)$_2$]$_2$ and the adduct deposits are present in agreement with the FTIR data.

The mechanism shown in Figure 4.5b is consistent with the IR and NMR data. Lewis acid base interactions between the aluminum alkyl group and DMAAs occur by electron sharing between the two nitrogens of DMAAs and two TMAI. Further interactions result in exchange reactions producing As(N(CH$_3$)$_2$)(CH$_3$)$_2$ and two molecules of Al(N(CH$_3$)$_2$)(CH$_3$)$_2$, which dimerize to form [Al(N(CH$_3$)$_2$)(CH$_3$)$_2$]$_2$. In the presence of more than a 2:1 ratio of TMAI to DMAAs, excess TMAI can attack the last dimethylamino group of the arsenic compound according to reaction r$_3$ to form an adduct and ultimately polymeric deposits. No trimethylarsenic is observed. The formation of bis Al-N bonded adducts is consistent with the absence of As(N(CH$_3$)$_2$)$_2$(CH$_3$) as the product of interaction between DMAAs and TMAI. As(N(CH$_3$)$_2$)$_2$(CH$_3$) could be produced if only one nitrogen of DMAAs interacted with TMAI.

The mechanism is also consistent with the reported results by Krannich et al., based on liquid phase reactions of DMAAs and TMAI at temperatures
between -95°C and 24°C. The bis Al-N bonded adduct is observed at -95°C and this adduct readily decomposes at room temperature to \( \text{As(N(CH₃)₂)₂(CH₃)} \) and \( \text{Al(N(CH₃)₂)(CH₃)}₂ \). The liquid phase interactions between \( \text{As(N(CH₃)₂)₂(CH₃)} \) and TMAI produce stable mono Al-N bonded adduct at room temperature.

Similar interactions are observed in the reaction between DMAAs and TMG as well as the reaction between DMAAs and TMIn. Figure 4.8a shows the vapor phase spectra of the DMAAs + TMG mixture after subtracting the contribution of the unreacted parents. The lower spectrum in Figure 4.8a is of the gas phase mixture of DMAAs and TMG as the pressure inside the gas cell reached 600 torr. Unlike the case of TMAI and DMAAs, the mixture shows a change in gas phase composition as a function of time. The spectrum in the top of Figure 4.8a, which is taken 60 minutes after mixing, represents the steady state gas phase mixture. Major peaks observed at this condition are in agreement with the spectrum of \( \text{[Ga(N(CH₃)₂)(CH₃)}₂ \) (see Table 4.3)\(^9\), which features strong bands at 498 cm\(^{-1}\), \( ν_{\text{Ga-N}} \), 902 cm\(^{-1}\) \( ν_{\text{Ga-N-C}} \) and peaks at 573, 536 and 727 cm\(^{-1}\) \( ν_{\text{as, s.}} \) and \( ρ \) Ga-CH₃ bonds). The minor bands, marked by an asterisk, represent the spectrum of \( \text{As(N(CH₃)₂)(CH₃)}₂ \), similar to that observed in the case of TMAI.

The IR spectrum of the mixture of TMIn and DMAAs after reaching steady state also indicates the formation of the dimer \( \text{[In(N(CH₃)₂)(CH₃)}₂ \) \(^9\) and a trace of \( \text{As(N(CH₃)₂)(CH₃)}₂ \). The spectrum of the indium dimer has two distinctive peaks of \( ρ \) N-CH₃ at 917 and 890 cm\(^{-1}\), a peak at 498 cm\(^{-1}\) due \( ν_{\text{In-N}} \), and peaks at 699, 509 and 482 cm\(^{-1}\) corresponding to \( ρ_{\text{In-CH₃}}, ν_{\text{as, In-C}} \) and \( ν_{\text{s, In-C}} \).

The "as mixed" spectra for both mixtures likely represent the formation of Lewis acid-base adducts similar to those observed in the mixture of DMAP with trialkyl group III (Section 4.4.1). However, in this case the adducts are formed.
by interactions of two group III atoms with two dimethylamine groups in DMAAs. Both spectra contain vibrational modes from the As-dimethylamino part of the adduct; i.e. a peak at 1264 cm\(^{-1}\) due to \(\nu_{C-N-C}\) (shifted from 1255 cm\(^{-1}\)) and bands from \(\rho_{CH_3}, \nu_{As-N-C}\) and \(\nu_{As-N}\) at 1030, 960 and 565 cm\(^{-1}\). The complete peak assignments of the adducts are given in Table 4.4.

Figure 4.9 shows the time evolution of consumption of TMG, DMAAs and generation of \([Ga(CH_3)\_2(N(CH_3)\_2)]_2\) in the gas cell. Initially, about 2 moles of TMG is consumed for every mole of DMAAs and the rate of consumption of TMG is faster than DMAAs. Once the system reaches steady state, about three moles of TMG have been consumed per mole of DMAAs. These observations agree with proposed complex gas phase exchange reactions between trialkyl group III and DMAAs as illustrated in Figure 4.5b. At time \(t = 0\), the equilibrium \(r_2\) is established resulting in a two to one consumption of TMG and DMAAs. At \(t > 0\), reactions \(r_3\) starts to evolve leading to formation of \([Ga(CH_3)\_2(N(CH_3)\_2)]_2\) and \(As(N(CH_3)\_2)(CH_3)_2\). Excess TMG immediately reacts with \(As(N(CH_3)\_2)(CH_3)_2\) through \(r_4\) to form a low vapor pressure adduct which readily condenses on the reactor wall. The reduction in TMG concentration disrupts the equilibrium \(r_1\) resulting in more consumption of DMAAs and TMG. The same mechanism also applies for mixtures of TMIn and DMAAs.
Figure 4.6  The infrared spectra of a) DMAAs, b) 3:1 mixture of TMAI and DMAAs, c) 2:1 mixture of TMAI and DMAAs. Figure b and c represent the spectra after subtracting excess DMAAs or TMAI contribution. The vibrational modes for As(N(CH₃)₂(CH₃)₂) are marked by asterix.
Figure 4.7  a) Proton and b) $^{13}$C NMR spectra of 2:1 mixture of DMAAs and TMAI.
Figure 4.8  

a) The infrared spectra of 1:2 DMAAs and TMG mixtures; the lower spectrum is recorded after mixing, the upper spectrum represent steady state conditions.

b) The infrared spectra of 1:2 DMAAs and TMIn mixtures; the lower spectrum is recorded after mixing, the upper spectrum represent steady state conditions.

Bands marked by (*) are from As(N(CH₃)₂)(CH₃)₂.
Figure 4.9  Time evolution of DMAAs (x), TMG (o) and \([\text{Ga(N(CH}_3)_2](\text{CH}_3)_2]\) (△) in the 2:1 mixture of TMG and DMAAs.
### Table 4.3: Table of infrared peak assignment of \([\text{M(N(CH}_3)_2\text{)}\text{R}_2\text{]}_2\), (M- Al, Ga and In, R - methyl or ethyl).

<table>
<thead>
<tr>
<th>([\text{Al(N(CH}_3)_2\text{)}\text{N(CH}_3)_2\text{]}_2)</th>
<th>([\text{Ga(N(CH}_3)_2\text{)}\text{N(CH}_3)_2\text{]}_2)</th>
<th>([\text{In(N(CH}_3)_2\text{)}\text{N(CH}_3)_2\text{]}_2)</th>
<th>Assignment *</th>
<th>([\text{Ga(C}_2\text{H}_5\text{)}\text{N(CH}_3)_2\text{]}_2)</th>
<th>Assignment **</th>
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<tbody>
<tr>
<td>1459</td>
<td>1461</td>
<td>1468</td>
<td>(\delta\ \text{N-CH}_3)</td>
<td>1471</td>
<td>(\delta\ \text{N-CH}_3)</td>
</tr>
<tr>
<td>1438</td>
<td>1448</td>
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<td>(\delta\ \text{N-CH}_3)</td>
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<td>(\delta\ \text{N-CH}_3)</td>
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<td>1408</td>
<td>1408</td>
<td>(\delta\ \text{N-CH}_3)</td>
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<td>(\delta\ \text{C-CH}_3)</td>
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<td>1231</td>
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<td>1138</td>
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<td>(\nu\ \text{C-N})</td>
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<td>(\nu\ \text{C-N})</td>
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<td>1049</td>
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<td>(\nu\ \text{C-N})</td>
<td>1046</td>
<td>(\nu\ \text{C-N})</td>
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<td>902</td>
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<td>(\rho\ \text{N-CH}_3)</td>
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<td>(\nu\ \text{M-N})</td>
<td>500</td>
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</table>

* Reference 98
** This work
Table 4.4. Adduct between DMAAs and TMG/TMI

<table>
<thead>
<tr>
<th>DMAAs + TMG</th>
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<th>DMAAs</th>
<th>DMASb</th>
<th>Assignment</th>
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<tr>
<td>1464</td>
<td>1460</td>
<td>1465</td>
<td>1463</td>
<td>$\delta_{N-CH_3}$</td>
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<td>1264</td>
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<td>1194</td>
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<td>460</td>
<td>-</td>
<td>-</td>
<td>$\nu_{M-N}$</td>
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* M = Sb or As
Table 4.5. IR bands assignment of other gas phase reaction products

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<th>Name</th>
<th>IR Peak (cm⁻¹)</th>
<th>Assignment</th>
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<tr>
<td>As(N(CH₃)₂)(CH₃)₂</td>
<td>1260</td>
<td>ν C-N-C</td>
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<td></td>
<td>950</td>
<td>ν As-N-C</td>
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<tr>
<td></td>
<td>832</td>
<td>ρ As-CH₃</td>
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<tr>
<td></td>
<td>580</td>
<td>ν As-C</td>
</tr>
<tr>
<td></td>
<td>564</td>
<td>ν As-N</td>
</tr>
<tr>
<td>As(N(CH₃)₂)(C₂H₅)₂</td>
<td>1240</td>
<td>ν C-N-C</td>
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<tr>
<td></td>
<td>949</td>
<td>ν As-N-C</td>
</tr>
<tr>
<td></td>
<td>713</td>
<td>ρ As-CH₂</td>
</tr>
<tr>
<td></td>
<td>564</td>
<td>ν As-C, ν As-N</td>
</tr>
<tr>
<td>Sb (CH₃)₃</td>
<td>812</td>
<td>ρ Sb-CH₃</td>
</tr>
<tr>
<td></td>
<td>525</td>
<td>ν Sb-C</td>
</tr>
<tr>
<td></td>
<td>517</td>
<td>ν Sb-C</td>
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<tr>
<td>Sb(N(CH₃)₂)(C₂H₅)₂</td>
<td>1226</td>
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<tr>
<td></td>
<td>950</td>
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<tr>
<td></td>
<td>758</td>
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<tr>
<td></td>
<td>512</td>
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<tr>
<td></td>
<td>494</td>
<td>ν Sb-N</td>
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4.4.3 Reactions of DMASb and trimethyl group III sources

Figure 4.10 compares gas phase IR spectra products of mixing a) TMAI+ DMASb, b) TMG + DMASb and c) TMIn + DMASb. The significant peaks observed after mixing TMAI+DMASb are attributed to $[\text{Al}(\text{N(CH}_3)_2)(\text{CH}_3)_2]_2$, identical to those produced in the mixture of TMAI and DMAAs. The peaks at 812, 525 and 517 cm$^{-1}$ are assigned to trimethylantimony (TMSb or Sb(CH$_3$)$_3$).$^{96,103}$ No other Sb-containing organometallic is observed in the spectra. The NMR analysis of the gas phase products agrees well with this observation. The proton NMR in Figure 4.11 shows peaks at + 2.06 and -0.59 ppm due to $[\text{Al}(\text{N(CH}_3)_2)(\text{CH}_3)_2]_2$ and a peak at + 0.59 ppm due to TMSb.$^{104}$

The reaction of TMG and DMASb produces $[\text{Ga(N(CH}_3)_2)(\text{CH}_3)_2]_2$ and TMSb. The infrared spectra (Figure 4.10b) agree well with the published data (see Table 4.2 and Table 4.5). The infrared experiments also show that for each DMASb consumed, three equivalents of TMAI or TMG are required. These observations suggest that the reactions of TMG/TMAI with DMASb may be summarized as follows:

$$3 \text{M(CH}_3)_3 + \text{Sb(N(CH}_3)_2)_3 \rightarrow \text{Sb(CH}_3)_3 + 1/2 [\text{M(CH}_3)_2(\text{N(CH}_3)_2)_2]_2 \quad \quad \text{M= Al, Ga.} \quad \quad (3.1).$$

This result is consistent with the results of liquid phase interactions between TMAI and DMASb.$^{105}$

The reaction of TMIn with DMASb also produces trimethylantimony, (see Figure 4.10c). The other product of the reactions is identified as $\text{In(N(CH}_3)_2)(\text{CH}_3)$; the spectra show a stronger peak of $\nu_{\text{In-N}}$ at 445 cm$^{-1}$ and weaker $\nu_{\text{In-C}}$ at 480 cm$^{-1}$ compared to the spectra of $[\text{In(N(CH}_3)_2)(\text{CH}_3)_2]_2$, which is observed in the reaction between TMIn and DMAAs. The single peak
due to $\nu_{\text{In-N-C}}$ at 914 cm$^{-1}$ is different from the two peaks observed at 918 and 890 cm$^{-1}$ for the In-dimer molecule formed in the mixture between TMIn and DMAAs (Figure 4.8b). Infrared spectroscopy on mixtures of different ratios of TMIn and DMASb conclude that for every two moles of DMASb consumed, three moles of TMIn are needed. The overall reactions between TMIn and DMASb may therefore be summarized as:

$$3 \text{In(CH}_3\text{)}_3 + 2 \text{Sb(N(CH}_3\text{)}_2\text{)}_3 \rightarrow 2 \text{Sb(CH}_3\text{)}_3 + 3 \text{In(CH}_3\text{)}(\text{N(CH}_3\text{)}_2\text{)}_2$$  (3.2)
Figure 4.10  The comparison of infrared spectra of a) TMAI + DMASb, b) TMG + DMASb and c) TMIn + DMASb. Bands marked by (*) are attributed to TMSb.
Figure 4.11  Proton NMR spectrum of the DMASb and TMAi mixture.
4.4.4 Reaction of triethylgallium with DMAAs and DMASb

Gas phase interactions of DMAAs and TEG form adducts through Lewis acid-base interactions between two N atoms with two Ga atoms, similar to DMAAs and TMG. Figure 4.11a shows the spectrum of the adduct which was taken immediately after the gas pressure reached 600 torr. The spectrum is relatively weak due to the low vapor pressure of the adduct. The \( \nu_{Ga-C} \) peak of triethylgallium at 544 cm\(^{-1}\) is shifted to 526 cm\(^{-1}\) due to the formation of the adduct with nitrogen. The positions of \( \nu_{Ga-C} \) as well as the other peaks corresponding to vibrations of Ga-ethyl are similar to those observed in the TEG + DMAP adduct described earlier in Table 4.2. The peak at 894 cm\(^{-1}\) and a shoulder peak at 957 cm\(^{-1}\) are correspondingly due to the \( \nu_{Ga-N-C} \) and \( \nu_{As-N-C} \) vibrational modes similar to those of TMG and DMAAs adducts.

The steady state spectra taken at 60 minutes show the formation of \([Ga(N(CH_3)_2)(C_2H_5)_2]_2\) molecules marked by (x) in Figure 4.12b. This molecule, which is observed as well in the steady state spectra of mixture between TEG and DMASb in Figure 4.12c, shows strong peaks due to \( \nu_{Ga-N-C} \) and \( \nu_{Ga-C} \) at 902 and 550 cm\(^{-1}\). The complete vibrational assignment is listed in Table 4.2. By analogy to the mixture of TMG and DMAAs, the other product observed is due to the \( As(N(CH_3)_2)(C_2H_5)_2 \) compound. The appearance of an As-C\(_2\)H\(_5\) species is evidenced by a strong peak at 713 cm\(^{-1}\) due to \( \rho_{As-CH2} \) and peaks around 550-570 cm\(^{-1}\) due to \( \nu_{As-C} \) similar to that observed in \( As(C_2H_5)_2Y \) (Y = Cl or Br).\(^{96}\) The As-N(CH\(_3\))\(_2\) vibrational modes appear at 564 and 950 cm\(^{-1}\) similar to those observed in the methyl analog compound. The peak assignment of this molecule can be found in Table 4.4.
Figure 4.12 The comparison of infrared spectra of a) TEG + DMAAs as mixed. b) TEG + DMAAs at steady state and c) TEG + DMASb at steady state. The (x) in the legend is the spectra of [Ga(N(CH₃)₂)(C₂H₅)₂]₂.
In the 2:1 mixture of TEG and DMASb, \( \text{Sb(N(CH₃)₂)(C₂H₅)₂} \) is observed as the other product analogous to the TEG and DMAAs case. The assignment of the peaks can be found in Table 4.5. Increasing the molar ratio of TEG/DMASb to 2.5 results in a decrease in the formation of \( \text{Sb(N(CH₃)₂)(C₂H₅)₂} \) and an increase in the formation of triethylantimony (\( \text{Sb(C₂H₅)₃} \)). It is likely that the reactions proceed similar to those observed in TMG and DMAAs. In the mixtures with \( \frac{\text{III/V}}{\text{V}} \leq 2 \), the interactions produce \( \text{Sb(N(CH₃)₂)(C₂H₅)₂} \) and \( \text{[Ga(N(CH₃)₂)(C₂H₅)₂]₂} \). In the mixture \( \frac{\text{III/V}}{\text{V}} \geq 2 \), extra TEG reacts with the last dimethylamino group of the Sb compound to form triethylantimony.

4.5 Discussion: adduct reactions and implications for OMCVD growth

The interactions between tris-dimethylamino group V sources and trialkyl group III sources are summarized in Table 4.6. Each cell in the Table contains information about the gas-phase products observed. Interactions between a trimethyl-group III source and DMAP result in the formation of an adduct. With DMAAs, an adduct is first generated and this is followed by the formation of \( \text{[M(N(CH₃)₂)(CH₃)₂]₂} \) and \( \text{As(N(CH₃)₂)(CH₃)₂} \). DMASb interactions are the strongest resulting in adduct formation and subsequent generation of trimethylantimony and group III dimers.

The Lewis acid base interactions between the nitrogen atoms and group III sources occurred almost immediately for each III-V combination studied. In the mixture containing DMAAs and DMASb, two nitrogen atoms on each molecule interacted with the group III source. The strength of the E-N bond energy is as follows: \( \text{P > As > Sb} \), while the strength of the Lewis acid is as follows: \( \text{Al > Ga > In} \).
Table 4.6 Summary of interactions between trialkyl group III and tris-dimethylamino group V sources

<table>
<thead>
<tr>
<th></th>
<th>DMAP</th>
<th>DMAAs</th>
<th>DMASb</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>Adduct</td>
<td>A, B</td>
<td>A, C</td>
</tr>
<tr>
<td>TMG</td>
<td>Adduct</td>
<td>A, B</td>
<td>A, C</td>
</tr>
<tr>
<td>TMI</td>
<td>Adduct</td>
<td>A, B</td>
<td>A* C</td>
</tr>
<tr>
<td>TEG</td>
<td>Adduct</td>
<td>A, B</td>
<td>A, B, C</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
A &= \text{Adduct} + [M(N(CH_3)_2)_2(R)]_2 \\
A^* &= \text{Adduct} + [M(N(CH_3)_2)_2(R)] \\
B &= E(N(CH_3)_2)_2R_2 \\
C &= ER_3
\end{align*}
\]

\[M = \text{Al, Ga, In} \]
\[E = \text{P, As, Sb} \]
\[R = \text{Me, Et.} \]
The difference in E-N (E = P, As, Sb) bond strength results in differences in product formation. In the case of DMAP, the interaction energy between group III and nitrogen is not enough to overcome the barrier of breaking the P-N bond, resulting in the formation of a stable Lewis acid base adduct, while in the case of DMASb, the Sb-N energy is low enough to facilitate the replacement of all of the amino groups with methyl groups.

The difference in the Lewis acid strength results in a change in the rate of product formation. Figure 4.13 illustrates the comparison of time evolution of the group III dimers formed in the reactions of trialkyl group III sources with DMAAs (Figure 4.13a) and with DMASb (Figure 4.13b). The reactions are fastest for TMAI and slowest for TMIn consistent with the relative strength of Al > Ga > In. The interactions of TMG is stronger than TEG consistent with the relative strength of the Lewis acidity between the two molecules due to the difference in steric effect.\textsuperscript{65}

The interactions between group III and group V sources are likely to affect OMCVD growth by lowering the growth rate and forming adduct deposits. The formation of low vapor pressure adducts, like those observed in DMAP, will result in the reduction of growth rate due to the decrease in the gas phase concentration of the sources. In growth with DMAAs, the formation of the group III dimer not only reduces the growth rate but also leads to an undesired change in the chemistry of the process. Since the relative bond energy of group III-N is higher than III-C, more energy is required to decompose the dimer molecule. Incomplete decomposition of this compound could lead to nitrogen and carbon incorporation which was observed in the growth of AlGaAs and AlInAs.\textsuperscript{58, 94} The group V-alkyl compounds are not preferable since they not only required higher temperature to decompose but also led to carbon incorporation into the film, especially in the growth of Al or Ga containing films.
Figure 4.13  Comparison of the rate of formation of the $[\text{M(N(CH}_3)_2(CH}_3)_2]_2$ in the mixture of trialkyl group III sources with a) DMAAs, b) DMASb. The group III sources are TMAI (x), TMG (○), TMIn (△) and TEG (o).
The adduct condensation and exchange reactions could lead to growth problems especially at the end of growth run as it was encountered in the growth of GaSb using TEG and DMASb. The volatile gas products from ligand exchange reactions continued to flow to the growing film even after the organometallics were switched to the vent line. Since the temperature of the wafer was still hot at the end of the run, this would result in post deposition growth. This effect is not desirable for growth of heterojunction devices.

4.6 Conclusions

Parasitic room temperature reactions between tris-dimethylamino group V compounds and trialkyl group III sources occurred via Lewis acid base interactions between a nitrogen atom from the dimethylamino group and the group III element. Reaction of DMAP with trialkyl group III sources resulted in the formation of low vapor pressure adducts between one of the nitrogen and trialkyl group III. In DMAAs and DMASb, the formation of low vapor adducts was followed by alkyl-amino exchange reactions resulting in the formation of a dimer [M(N(CH₃)₂(CH₃)₂]₂ and As(N(CH₃)₂(CH₃)₂) or Sb(CH₃)₃, respectively.

The formation of low vapor pressure adducts could disturb the stoichiometry of the growth and lead to formation of particulates which might affect the film morphology. Ligand exchange reactions observed in mixtures containing DMAAs or DMASb produce reaction products which are more stable at high temperature compared to the starting reagents.¹⁰⁶ Incomplete decomposition of these molecules will lead to an increased possibility of carbon and nitrogen incorporation in the film. Therefore, the use of tris-dimethylamino group V sources for OMCVD growth should be restricted to low pressure conditions and short mixing time between group III and V sources.
Chapter 5:

Conclusions and Recommendations for Future Work

This thesis described the implementation of new FTIR techniques in 3 OMCVD applications: a) *in-situ* concentration monitoring, b) *in-situ* gas-phase decomposition studies of new sources tris-dimethylamino group V compounds and c) *in-situ* investigation of gas phase interactions between group III trialkyls and the new group V sources.

Application of fluoride fiber optics based FTIR is suitable for *in-situ* concentration measurement both in the gas delivery line and directly from a reactor. The technique is based on infrared absorption of organometallic reagents and hydride gases in the mid-IR region. The optimum performance is achieved using an InSb detector and a seven fluoride fiber bundle system. Typical detection limits for a single 10 cm pathlength transmission and one second scan time range from 0.05 to 0.005 torr. These limits are acceptable for organometallic vapor pressure measurements. Design of a multiple path cell and optimization of the fiber optic throughput would further improve the detection limit and reduce the gas cell size. An order of magnitude improvement in the detection limit by longer scan time allows direct *in-situ* monitoring of chemical species in a growth reactor. This is very useful for detecting delivery problems such as condensation, adduct formation and variation caused by unsaturated condition inside a bubbler. The comparison study between the FTIR and the ultrasonic techniques demonstrates the advantage of the FTIR as a chemically selective technique for accurate
measurement of organometallic concentrations. A simple residence time model may be used in conjunction with the FTIR technique to identify problems of wall condensation and chemical interactions.

A novel approach for in-situ studies of gas phase decompositions relevant to typical CVD conditions has been successfully developed based on coupling a pyrolysis tube reactor and the FOB-FTIR system. The set-up was used for studying the gas phase decomposition of tris-dimethylamino-phosphine, -arsine and stibine precursors for OMCVD of InP, GaAs, InSb and related compounds. Pyrolysis studies showed that the reagents primarily decomposed through homolysis of the central atom (E=P, As, Sb)-dimethylamine bond producing dimethylaminyl radicals. Fifty percent decomposition temperatures for the phosphorous, arsenic and antimony were: 495°, 385° and 325°C. This temperature trend is in agreement with the relative strengths of the E-N bonds. The decomposition occurs without detectable side reactions leading to the formation of other organogroup V compounds. The results were confirmed by molecular beam mass spectroscopy. Interactions of dimethylaminyl radicals and hydrogen produce stable products of dimethylamine, methyl-methyleneimine, methane, methyleneimine and ammonia. At temperature higher than 550°C, dimethylaminyl radicals decomposed to form ammonia and methane. This reaction pathway could lead to parasitic nitrogen and carbon incorporation into the film during OMCVD growth.

The novel in-situ FTIR methods was combined with ex-situ NMR spectroscopy in successful investigations of gas phase interactions between trisdimethylamino group V compounds and trialkyl group III molecules. Parasitic room temperature reactions occurred via Lewis acid-base interactions between a nitrogen atom from a dimethylamino group and the group III elements. Reaction of DMAP with trialkyl group III sources results in the formation of low
vapor pressure adducts. In the case of DMAAs and DMASb, the formation of low vapor pressure adducts is followed by alkyl-amino exchange reactions.

The formation of these condensable adducts disturbs the stoichiometry of the growth and could potentially lead to formation of particulates which may effect the film morphology. Ligand exchange reactions observed in mixtures containing DMAAs or DMASb are not desirable since they produce reaction products which are more stable at high temperature compared to the starting species, which increases the possibility of carbon and nitrogen incorporation. The results conclude that the use of tris-dimethylamino group V sources should be restricted for low temperature OMCVD growth with limited room temperature interactions between group III and V sources.

Further investigations of other potential applications of FOB-FTIR in a CVD process are recommended. For example, direct monitoring of an OMCVD reactor FOB-FTIR is useful for exploring the gas phase decomposition chemistry of organometallic sources during an actual growth process. The FOB-FTIR could be used as well for other in-situ monitoring applications such as film thickness measurement and surface chemistry studies under growth conditions. When using new alternative precursors, the possibility of interactions needs to be explored. In this thesis, tools for analyzing such interactions have been developed.
Appendix A:

Analysis of the Gas Cell for High Temperature Decomposition Studies of Organometallics Reagents Relevant to CVD

A.1 Performance test: decomposition of TMG and TMIn

The performance of the gas cell is tested with the decomposition of trimethylgallium (TMG) and trimethylindium (TMIn). TMG and TMIn are chosen because the reaction mechanisms are understood and their pyrolysis has been explored by a variety of other spectroscopy techniques. Both TMG and TMIn decompose in hydrogen according to a free radical mechanism to produce methane as the main product.3

The experiments were carried out in the Crystal Specialty system (Figure 2.1a) using the gas cell shown in Figure A.1. The concentration of the organometallic precursor was maintained in the range 1.5-2.0 × 10⁻⁴ mol/l, the carrier gas flow rate was set at 60 sccm and the cell pressure was kept at 600 torr. The other conditions used in this experiment were similar to those described in Chapter 3.

Figure A.2a shows spectra of gas-phase species at a low temperature (200°C) before TMG decomposition commences, and at a high temperature (650°C) after the reagent has been completely decomposed to methane. Besides the absorbance at 2800-3000 cm⁻¹ from methyl vibrational stretching modes, the
other significant absorbance for TMG is the deformation mode at 1211 cm\(^{-1}\). The vibrational mode of the Ga-C bond is at 580 cm\(^{-1}\) and cannot be monitored with the fiber.\(^{86}\) Nevertheless, the degree of conversion of TMG to methane may be monitored by following the intensities of the bands at 2918 and 1211 cm\(^{-1}\), as well as those for methane.

Figure A.2b shows the change in the peak height at 1211 cm\(^{-1}\) and 1306 cm\(^{-1}\) as a function of temperature. The initial slow decrease in the peak height is due to the temperature effect on the gas expansion. A sharp decrease in the peak at 375 to 500°C is due to decomposition of the precursor. This decrease is also accompanied by the formation of methane at 1304 and 3016 cm\(^{-1}\). At temperatures higher than 500°C, the peak at 1211 cm\(^{-1}\) is not completely gone but slowly decreases as a function of temperature. This signal is attributed to undecomposed TMG accumulated close to the low temperature IR window (held at 50°C).

A simple two-cell reactor model is used to interpret decomposition data. The first cell is a well-mixed reactor region, where the decomposition takes place, and the second is a dead volume section for the low temperature region closed to the windows. The relative volume of the well mixed region is about 2.5 times the dead volume region. The decomposition data are obtained by subtracting the contribution from the dead volume section. Figure A.3a compares the corrected pyrolysis data from the gas cell with published results. The data designated by (O) are generated by sampling gas products from an OMCVD reactors using an \textit{ex-situ} FTIR technique\(^{22}\) and the results marked (\(\Delta\)) stem from a mass spectroscopy study of pyrolysis in a heated tube\(^{107}\). The good agreement between data from \textit{in-situ} IR experiments and published data, validates the use of the \textit{in-situ} gas-cell.
Figure A.1  Schematic diagram of the gas cell.
Figure A.2  

a) Spectra of TMG in H₂ at 200°C (bottom) and 650°C (top).

b) TMG decomposition observed by monitoring the intensity of the 1214 cm⁻¹ band and the formation of methane is determined from the evolution of the 1304 cm⁻¹ band.
Figure A.3  
a) Comparison of TMG decomposition data obtained at 600 Torr (+) with IR results of Denbaars et al.,22 (O) and mass spectroscopy results of Larsen et al.107 (Δ).

b) Comparison of TMI decomposition data obtained at 600 Torr (+) with mass spectroscopy results of Buchan et al. 108 (O).
Similar results are obtained for the pyrolysis of TMIn. TMIn also reacts to methane according to free radical mechanisms. The IR data again compare well with results obtained with mass spectroscopy investigations as shown in Figure A.3b.\textsuperscript{108} In the next section, the gas cell is used for looking at the decomposition of a new aluminum precursor.

### A.2 Decomposition Study of a New Organoaluminum Source: TTBAI

Tri-tertiarybutylaluminum (TTBAI) is a new organoaluminum source which has recently been used successful for the growth of high purity aluminum films by low pressure CVD.\textsuperscript{35} The compound is attractive for OMCVD of III-V compound semiconductors. In this section, the \textit{in-situ} FTIR technique is used to study the gas phase decomposition of TTBAI.

The experiment was carried out in the Lincoln Laboratory OMCVD system (Figure 2.1b). The gas cell is placed in the vent line of delivery system. KBr windows were used in this study, and the gas cell was placed directly inside the sample compartment of the FTIR spectrometer, equipped with a TGS detector. The set-up allowed analysis of infra-red spectra covering most of the finger print region from 4000 to 400 cm\textsuperscript{-1}. The pressure inside the gas cell was kept at = 1 atm. The hydrogen flow rate was set to 70 sccm and the flow rate of TTBAI was about 2 \textmu mol/min.

Figure A.4 shows the evolution of infrared spectra of TTBAI in hydrogen for the temperature range of 150 to 300°C. The spectrum at 150°C represents the undecomposed TTBAI, which features peaks at 585 cm\textsuperscript{-1} (\textit{v}_{\text{Al-C}}), at 803 cm\textsuperscript{-1} (\textit{\rho}_{\text{C-H}}), peaks at 1400-1500 cm\textsuperscript{-1} (\textit{\delta}_{\text{C-H}}) and peaks around 2800-3000 cm\textsuperscript{-1} (\textit{v}_{\text{C-H}}). The
TTBAI source used in this study is contaminated with isoctane. As discussed in Section 2.4, the appearance of this compound results in an increase in the peak intensity at 2960 cm$^{-1}$ relative to 2847 cm$^{-1}$. The presence of this hydrocarbon should not change the results since the species is quite stable under the condition investigated. 109

As the temperature is increased, the signals of TTBAI at 2847, 803 and 585 cm$^{-1}$ decrease while new peaks of isobutene at 890, 1667 and 3100 cm$^{-1}$ and of isobutane at 2967 cm$^{-1}$ are observed 75. No other species are detected. Figure A.5 shows decomposition products as a function of temperature. The decomposition product peak height is converted into concentration based on absorptivity estimated from a reported absorbance data 75. The peak at 2847 cm$^{-1}$ is used to represent the parent molecule, the peak at 890 cm$^{-1}$ represents isobutene and the peak at 2967 cm$^{-1}$ is for isobutane.

The decomposition of TTBAI starts at temperatures as low as 175°C and the decomposition is completed at 265°C. The only observed gas-phase decomposition products are isobutane and isobutene; Al metal is deposited on the gas cell wall. About equal amounts of isobutane and isobutene are observed as products of decomposition. This observation suggests that the TTBAI starts to decompose by homolysis leading to the formation of isobutyl radicals:

$$\text{Al(C}_4\text{H}_9)_x \rightarrow \text{Al(C}_4\text{H}_9)_{x-1} + \text{C}_4\text{H}_9\cdot$$

(A.1),

where $x = 1, 2$ or $3$. Isobutyl radicals are likely to attack the unreacted TTBAI molecule abstracting hydrogen from the isobutyl group and leading to the formation of isobutane and isobutene:

$$\text{Al(C}_4\text{H}_9)_x + \text{C}_4\text{H}_9\cdot \rightarrow \text{Al(C}_4\text{H}_9)_{x-1} + \text{C}_4\text{H}_{10} + \text{C}_4\text{H}_8$$

(A.2).

The isobutyl radical can also react with other isobutyl radicals according to:

$$\text{C}_4\text{H}_9\cdot + \text{C}_4\text{H}_9\cdot \rightarrow \text{C}_4\text{H}_{10} + \text{C}_4\text{H}_8$$

(A.3).

No formation of isooctane (C$_8$H$_{18}$), which may be produced through
recombination of two isobutyl radicals, is observed. This is consistent with the slower rate of the recombination reaction compared to A.3 reported by Warnatz.\textsuperscript{109}

The role of hydrogen radicals in the decomposition is minimal at this low temperature. This is consistent with a sensitivity analysis; showing that the reaction rate between isobutyl radicals and hydrogen molecules to form hydrogen radicals and isobutane\textsuperscript{110} is much slower than the rate of A.3 at these operating conditions. The IR spectra of the decomposition product shows no evidence of Al-H (1700-1800 cm\textsuperscript{-1})\textsuperscript{5}, which indicates that the β-hydride elimination pathway is also not detectable.

The decomposition data of TTBAI is modeled by assuming a first order decomposition and the results are shown in Figure A.5. The model assumed a pre-exponential value of 10\textsuperscript{13} sec\textsuperscript{-1}. The calculated activation energy based on the model is 32.3 kcal/mole.
Figure A.4  *In-situ* infrared spectra of TTBAI decomposition in hydrogen at various temperatures.
Figure A.5 The product of decomposition of TTBAI as a function of temperature: TTBAI (Δ), isobutane (○) and isobutene (×). The line used for TTBAI is based on first order reaction model of TTBAI.
References:


List of Publications


