Pyrolysis Studies of the Single-Source GaAs Precursors $[Me_2Ga(\mu\text{-As-}i\text{-Pr}_2)]_3$, $[Me_2Ga(\mu\text{-AsMe}_2)]_3$, $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$, and $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$

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Pyrolysis of the single-source GaAs precursors $[Me_2Ga(\mu\text{-As-}i\text{-Pr}_2)]_3$ (1), $[Me_2Ga(\mu\text{-AsMe}_2)]_3$ (2), $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ (3), and $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ (4) was studied at 1×10^{-2} Torr in the presence of H_2 and He carrier gases over the temperature range 150–600 °C in a heated quartz tube. The trimeric precursors, 1 and 2, reacted at temperatures below 150 °C to produce diarsines, making them unsuitable for film growth. Similar reactions were not observed for the dimeric precursors 3 and 4. The results for ligand loss were consistent with β-H elimination, intramolecular coupling, and intermolecular coupling pathways. Loss of *t*-Bu ligands from 3 and 4 was observed to begin at 325 °C. The onset of methyl ligand loss from 3 was observed at 425 °C, while the ethyl ligands of 4 began to be eliminated at 350 °C, indicating that low-temperature growth of stoichiometric GaAs should be possible from 3 and 4.

Introduction

In previous publications we have reported the preparation of a number of compounds of the type $(L_nMEL'_n)_x$, where M and E are the group 13 and 15 (formerly III and V) elements, respectively, and L_n and L'_n are ligands, which may be thermally eliminated. The M–E bonds are of the two-center, two-electron σ type.[1] The potential use of these compounds as single-source precursors to III–V semiconductors is currently being investigated. We have recently reported the use of $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ as a single-source precursor to epitaxial GaAs films at 475–525 °C and 5×10^{-6} Torr. During film growth, the compound was sublimed at 135 °C, and the deposition process was done on a substrate that was radiantly heated from the underside.[2] Not all precursors of the type $(L_nMEL'_n)_x$ however give such promising results. For example film growth cannot be reproducibly performed using $[Me_2Ga(\mu\text{-As-}i\text{-Pr}_2)]_3$.

The effort involved in synthesizing, purifying, and evaluating potential precursors demands that a rational approach to precursor development be taken. An understanding of precursor decomposition and how it influences film properties is vital to the development of guidelines for the design of single-source precursors. Decomposition routes of the conventional group-13 and -15 precursors Me_3Ga and AsH_3 and related compounds have been investigated using isotopic labeling and mass spectrometry.[3-8] Here we report mass spectrometric studies of the pyrolysis of the single-source precursors $[Me_2Ga(\mu\text{-As-}i\text{-Pr}_2)]_3$ (1), $[Me_2Ga(\mu\text{-AsMe}_2)]_3$ (2), $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ (3), and $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ (4).

Experimental Section

A system was built that allowed precursor decomposition to be studied at pressures of 1×10^{-2} Torr and below (Figure 1). This allowed simulation of the environment in which we deposited GaAs films in a separate apparatus.[2] The system was constructed of stainless steel, and all connections were stainless steel vacuum fittings unless otherwise indicated. The compound of interest was held within a saturator. The saturator and all transfer lines downstream of it were contained in a thermostated oven, which provided the heat necessary to volatilize the compounds that are solids at room temperature. Hydrogen or helium could be leaked into the system as a carrier gas. The carrier gas and volatilized compound flowed into a 4.0-mm i.d. × 28-cm long quartz reaction tube situated in a furnace. In some experiments the surface area of the reactor was doubled by packing it with quartz fragments. The furnace temperature was manipulated using a programmable temperature controller. The reactor effluent was fed directly into a UTI 100C quadrupole mass spectrometer utilizing 70-eV electron impact (EI) ionization for compounds 1 and 3. The mass range was limited to 300 amu, thus preventing observation of the dimeric (3) or trimeric (1) species. Selected mass peaks were monitored by a computer as the furnace temperature was ramped. For compounds 2 and 4 the reactor effluent was fed into a Hewlett-Packard (HP) 5970B mass selective detector that had been modified by replacing the supplied Balzers TPH 050 turbomolecular pump with an Edwards Model 100 diffusion pump in order to accommodate larger gas loads. Several experiments for compounds 1 and 3 were repeated using the HP instrument in order to verify that consistent results could be obtained. The HP mass spectrometer also utilized a quadrupole and 70-eV EI ionization but could scan a mass range of 10–800 amu. The data acquisition system allowed the entire mass range to be monitored as the furnace temperature was ramped.

A typical experiment was as follows: First the system was evacuated with a mechanical pump. The oven was then brought to the desired temperature, and the furnace was brought to its initial temperature and allowed to equilibrate. The oven was maintained at temperatures as high as 140 °C for compounds 1 and 4, 145 °C for compound 3, and 75 °C for compound 2. The low temperature for compound 2 was required to inhibit decomposition during sublimation as will be discussed later. The saturator was then opened and carrier gas flow was initiated. The carrier gas flow rate was such that pressures of $(1\text{–}10) \times 10^{-6}$ Torr

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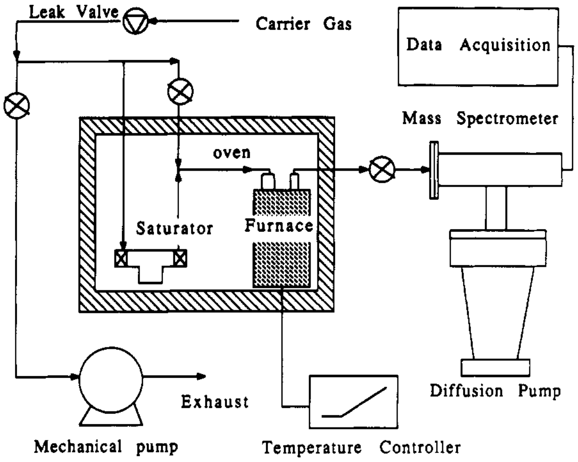

Figure 1. Pyrolysis apparatus.

Table I. Selected Mass/Charge Ratios, Their Corresponding Ion, and Assigned Species for the Pyrolysis of $[Me_2Ga(\mu\text{-}As\text{-}i\text{-}Pr_2)]_3$ (1), $[Me_2Ga(\mu\text{-}AsMe_2)]_3$ (2), $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ (3), and $[Et_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ (4)

mass/ charge ratio	ion	assigned species[a]
16	CH_4^+	methane; 1, 2, 3[b]
25	C_2H^+	ethene; 2
30	$C_2H_6^+$	ethane; 2, 4
42	$C_3H_6^+$	propene; 1
43	$C_3H_7^+$	*i*-propyl ligand; 1
43	$C_3H_7^+$	isobutane; 3, 4
44	$C_3H_8^+$	propane; 1
56	$C_4H_8^+$	isobutene; 1, 3, 4
57	$C_4H_9^+$	*t*-butyl ligand; 3, 4
58	$C_4H_{10}^+$	isobutane; 1
69	Ga^+	Ga; 1, 2, 3, 4
70	GaH^+	GaH; 4
71	Ga^+; $C_5H_{11}^+$	Ga; 2,3-dimethylbutane; 1
72	GaH^+	GaH; 4
84	$GaCH_3^+$	GaMe; 1
86	$GaCH_3^+$; $C_6H_{14}^+$	GaMe; 2,3-dimethylbutane; 1
120	$(CH_3)_3As^+$	trimethylarsine; 2
195	$C_3H_7As_2H_2^+$	tetraisopropyldiarsine; 1
204	$(C_3H_7)As^+$	triisopropylarsine; 1
210	$(CH_3)_4As_2^+$	tetramethyldiarsine; 1

[a] See text for complete details. [b] Pyrolyzed precursor compounds that generated the *m/e* signal.

(measured with an ionization gauge) were obtained in the mass spectrometer. A capacitance manometer was used to determine that these carrier flow conditions gave a pressure of approximately 10^{-2} Torr in the reactor. After stable signals were obtained by the mass analyzer, the furnace temperature was ramped at a rate of 1 °C/s. An experiment was also run at 0.5 °C/s for 3, giving identical results to the faster ramp, indicating that the residence time of reactants in the heated region was insignificant relative to the rate of temperature increase. It is important to note that the extent of a reaction at a specific temperature is a function of residence time provided the process is irreversible. This implies that a ligand, which shows only partial conversion at a temperature presented here (at a residence time of less than 1 s), would be completely reacted if the compound were held for a sufficiently long period of time at the same temperature. Monitoring a complete cycle of 12 masses took just over 2 s for the UTI instrument. Monitoring the entire mass range of the HP instrument required slightly less than 3 s.

Results

Table I summarizes some of the peaks monitored for 1–4 and the species from which they originated. Peak assignments were based on standard mass spectral tables for hydrocarbons, expected products, and knowledge of the precursor structure. The mass/charge (*m/e*) signals selected for presentation represent the most intense, unique peak of a species whenever possible. In the cases where overlap occurred, the relative amounts of each species present were considered and additional peaks were monitored to confirm the assignments. For example, during the decomposition of 1 the concentrations of isobutane and 2,3-dimethylbutane were small compared to the concentration of propene. Thus, at its greatest, the combined contribution to the *m/e* 42 signal from 2,3-dimethylbutane and isobutane was less than 13% of the contribution from propene and could therefore be ignored.

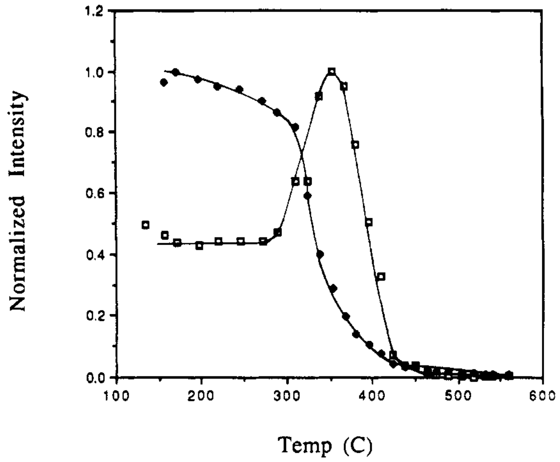

Figure 2. Triisopropylarsine (□) and tetraisopropyldiarsine (♦) signals from 1 as a function of the pyrolysis funace temperature.

Several reaction pathways are open to the hydrocarbon ligands on the single-source precursors. The simplest type of ligand loss process would be homolytic fission to yield hydrocarbon radicals. The probability of the radicals then recombining or reacting in the gas phase to form stable products is very small as the mean free path was on the order of the reactor diameter under the experimental conditions. Intermolecular reactions between surface-bound species and a gas-phase component or at the surface between two surface-bound species would be the more likely fate of radicals. This is supported by the fact that the results were unaltered in experiments where the H_2 carrier gas was replaced with He (see below), indicating a lack of gas-phase radical chemistry. Ligands containing a β-H such as *i*-Pr, *t*-Bu, and ethyl are expected to undergo β-elimination reactions. The products of β-elimination would be an olefin and a metal hydride. The final, anticipated ligand loss pathway involves an intramolecular coupling of ligands on the same metal center. Saturated hydrocarbon products would be the result of such a process.

Reactions involving the Ga–As bonds may also occur. These can result in species which retain the 1:1 stiochiometry of the precursor. For example the oligomers may decompose to form monomers. Alternatively, the 1:1 stiochiometry of the precursor may be destroyed.

The trimeric precursors, 1 and 2, reacted to form nonstoichiometric gallium and arsenic species at low temperatures. One of the products of this fragmentation was a volatile diarsine species. *The toxicology of diarsines and alkylarsines has been poorly studied, but their similarity to AsH_3 is clear. all manipulations and processing should be carried out in a drybox or in a well-ventilated hood.* Procedures for the manipulation of AsH_3 have been described.[9,10] Mass spectra obtained during the decompo-

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[9] Drake, J. E.; Riddle, C. *Inorganic Synthesis*; Cotton, F. A., Ed.; McGraw-Hill Book Co.: New York, 1972; Vol. XIII, pp 14–17.

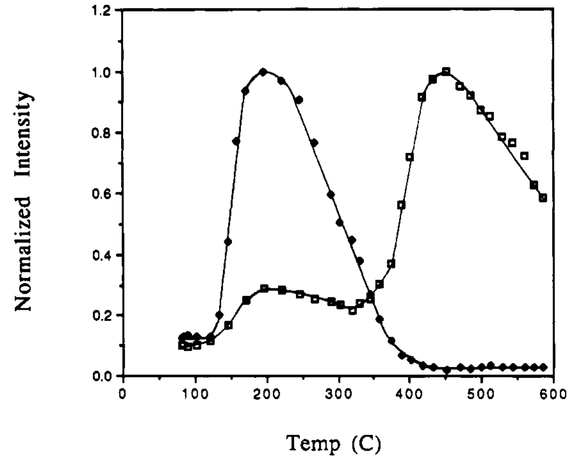

Figure 3. Trimethylarsine (□) and tetramethyldiarsine (♦) signals from 2 as a function of the pyrolysis furnace temperature.

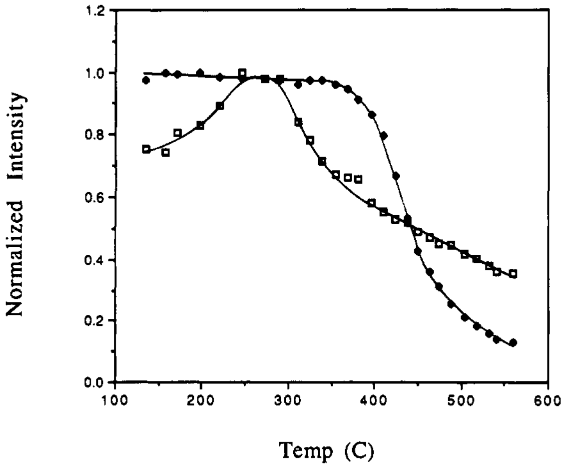

Figure 4. Ga (□, mass 69) and isopropyl ligand (♦) signals from 1 as a function of the pyrolysis furnace temperature.

sition of 1 and 2 demonstrate the presence of diarsines.[11] At higher temperatures trialkylarsines (triisopropylarsine and trimethylarsine) were formed. Figures 2 and 3 present the diarsine and trialkylarsine signals from 1 and 2, respectively, during pyrolysis. Diarsine formation began to occur at temperatures below the initial ramp temperature (150 °C) for 1. For compound 2 the ramp was begun at 100 °C and diarsine formation could be seen to commence at 125 °C. The tetramethyldiarsine signal in Figure 3 is representative of results for freshly prepared samples of 2. After compound 2 was stored at room temperature for several weeks, a tetramethyldiarsine signal was observed at a reactor temperature of 100 °C when the saturator was opened. Slow precursor decomposition to diarsines, at room temperature, was observed for both 1 and 2. The diarsine signal intensity at 150 °C for 1 and 100 °C for "aged" 2 could be reduced by evacuating the saturator, indicating the relative volatility of the diarsines. The signal intensity could then be restored by maintaining the saturator in a drybox for several weeks. The trialkylarsine signals increase in Figures 2 and 3 as the diarsine signals attenuate suggesting that the diarsines were precursors to the trialkylarsines.

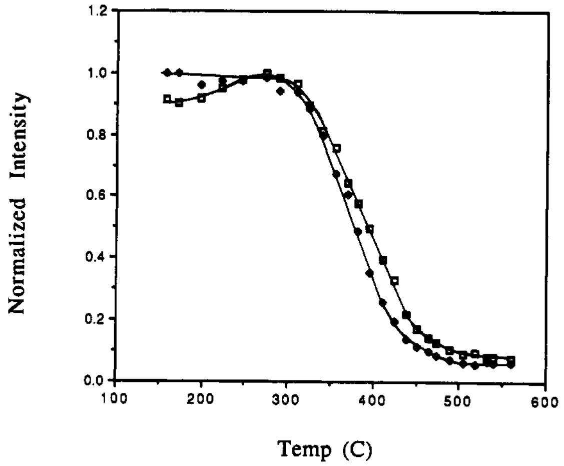

Figure 5. Ga (□, mass 69) and tertiarybutyl ligand (♦) signals from 3 as a function of the pyrolysis furnace temperature.

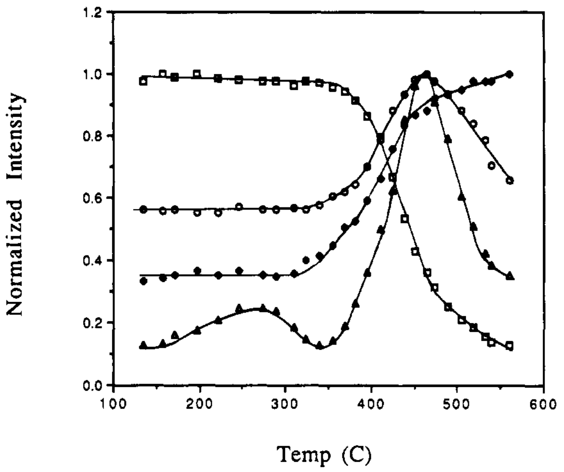

Figure 6. Isopropyl ligand (□), propene (♦), propane (○), and 2,3-dimetylbutane (△) signals from 1 as a function of the pyrolysis furnace temperature.

Further evidence for the fragmentation of Ga–As bonds of the trimeric compounds is found in Figure 4. Figure 4 demonstrates there is no clear correlation between the *i*-Pr ligands that originated on As and the Ga signal, suggesting the volatile species that originated from 1 did not all contain Ga–As bonds. Similar results (not shown) were found for 2, the final attenuation of the Ga signal was independent of the behavior of the arsenic-containing species trimethylarsine and tetramethyldiarsine.[11]

In contrast to the trimers 1 and 2, the dimeric precursors 3 and 4 showed no evidence of diarsine or trialkylarsine formation during pyrolysis. Figure 5 is representative of the results seen with the dimers and demonstrates that the volatile species from 3 consisted of a Ga–As moiety. The parallel behavior of the signals indicates that Ga atoms and the alkyl ligand associated with arsenic were contained in a single species.

For precursor 1, the hydrocarbon decomposition products (not all are shown) included propene, propane, methane, and four- and six-carbon species that were most likely isobutene, isobutane, and 2,3-dimethylbutane (Figure 6). The predominant species originating from the isopropyl ligand was propene, with lesser amounts of propane and the other products being formed. At 475 °C the ratio of propene:propane:2,3-dimethylbutane:isobutene:isobutane was estimated to be 100:50:10:1:1. Methane was also formed, with the onset of formation observed near 350 °C,[11] but it was difficult to determine the amount of

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[10] *The Merck Index*, 10th ed.; Windholz, M., Budavari, S., Blumetti, R. F., Otterbein, E. S., Eds.; Merck and Co. Inc.: Rahway, NJ, 1983; pp 117–118.

[11] Miller, J. E. Ph.D. Dissertation: University of Texas, Austin, TX, 1992.

methane relative to the other products due to the presence of background peaks. Doubling the surface area of the reactor during the pyrolysis of 1 did not alter the results. The pyrolysis results were independent of the H_2 or He carrier gas.

Figure 6 shows that the attenuation of the *i*-Pr signal for 1 coincided with the formation of propene, propane, and 2,3-dimethylbutane. The propene was likely formed through a β-H elimination mechanism that yielded the unsaturated product and provided H for the formation of propane via intramolecular coupling between a hydride ligand an *i*-Pr ligand. An analogous β-H elimination reaction has been demonstrated to occur during the decomposition of *tert*-butylarsine (t-$BuAsH_2$),[12] and the analogous coupling reactions have been postulated.[6,12] An intramolecular coupling of two *i*-Pr ligands would account for the formation of 2,3-dimethylbutane. The small peak from 200 to 300 °C in the 2,3-dimethylbutane signal was actually caused by Ga–Me fragments. At higher temperatures β-H elimination was the favored pathway and most *i*-Pr ligands underwent elimination in preference to the coupling reactions, thus accounting for the decrease in propane and 2,3-dimethylbutane at temperatures above 475 °C. The reasons for this preference may be either thermodynamic or kinetic. Competition with methyl groups of $Ga(Me)_2$ for H was probably not a factor in the propene/propane ratio since the data show propane and 2,3-dimethylbutane both reached maxima at the same temperature. Furthermore, the *i*-Pr ligands of i-Pr_2AsH behaved identically in similar pyrolysis experiments.[11]

Coupling reactions involving methyl and *i*-Pr ligands account for the formation of C_4 products. The attenuation of the tetraisopropyldiarsine signal coincided with the appearance of the C_4 products.[11] Furthermore the only *m*/*e* signals not affected by closing the saturator containing the compound when the furnace temperature reached 350 °C were those associated with the diarsine, the trialkylarsine, and the C_4 products. These results suggest that the conversion of the diarsine to the trialkylarsine yielded a reactive As(*i*-Pr) species that in turn produced the C_4 products. Alternately, the *i*-Pr contribution to the C_4 products could have arisen from the product formed by the remaining fragments of trimers that had decomposed in the saturator to form tetraisopropyldiarsine. The methyl ligands required for C_4 production were contributed either by this second product of diarsine formation or by compound 1 that had remained intact.

The hydrocarbon decomposition products from 2 were methane, ethane, and ethene with roughly equivalent amounts of each product being formed. The temperature at which the methyl ligands began to be lost from the Ga atoms and As atoms can be inferred as 350 and 450 °C, respectively. (These temperatures refer to the maxima in the signals for Ga and trimethylarsine.[11]) Since no β-H atoms were present, free-radical mechanisms were probably responsible for the methane production. However, the use of He carrier gas did not alter the results.

Figure 7 demonstrates the *t*-Bu ligands of 3 behaved similarly to the *i*-Pr ligands of 1. The attenuation of the *t*-Bu signal and the corresponding formation of isobutene and isobutane can clearly be seen. At 425 °C roughly equal amounts of isobutene and isobutane were formed. Small amounts of five and eight-carbon species may have also been formed. However, these products could not be observed due to a lack of unique, measurable peaks. Isobutene formation likely occurred via β-H elimination, while isobutane formation occurred through an intramolecular coupling process. As with 1, β-H elimination was the preferred pathway at high temperatures. Doubling the surface area or substituting He for H_2 did not significantly alter the pyrolysis results.

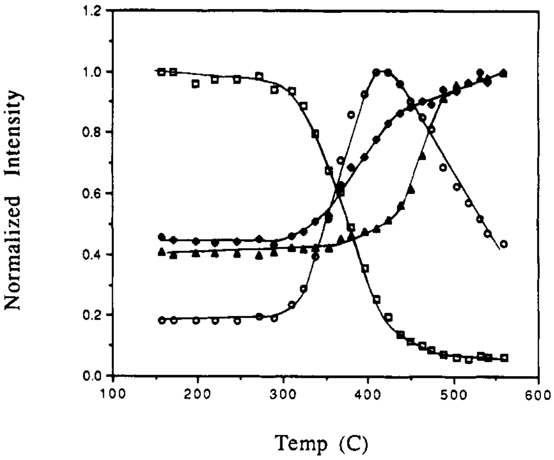

Figure 7. *tert*-Butyl ligand (□), isobutene (♦), isobutane (○), and methane (△) signals from 3 as a function of the pyrolysis furnace temperature.

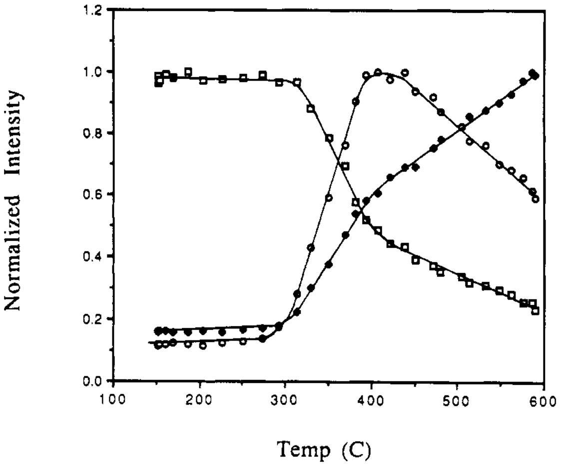

Figure 8. *tert*-Butyl ligand (□), isobutene (♦), and isobutane (○) signals from 4 as a function of the pyrolysis furnace temperature.

Figure 7 also shows the onset of methane formation of 3 occurred at 425 °C, ca. 100 °C above the temperature that the *t*-Bu ligands began to react. The amount of methane relative to the other products was again difficult to determine. The H required for methane formation was probably provided by the β-H elimination of *t*-Bu ligands. Interestingly, methane production began at the same temperature at which the intramolecular coupling reaction that produced isobutane began to diminish. However, the *t*-Bu ligands of t-Bu_2AsH behaved identically in similar pyrolysis experiments,[11] suggesting that although methane production may have been facilitated by the fall in isobutane production, it was not likely the cause of the decline.

The pyrolysis results obtained for the *t*-Bu ligands of 4 (Figure 8) are nearly identical to the results obtained for the *t*-Bu ligands of 3, and similar mechanisms should be operative. As with 3, at 425 °C roughly equivalent amounts of isobutene and isobutane were formed. Due to overlap with peaks from the *t*-Bu ligands, the ethyl ligands were difficult to track through mass spectrometry. However, similar pyrolysis experiments conducted at atmospheric pressure, so that samples could be collected for gas chro-

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[12] Marking, R. H.; Gladfelter, W. L.; Jensen, K. F. *Chem. Mater.* **1990**, 2, 499.

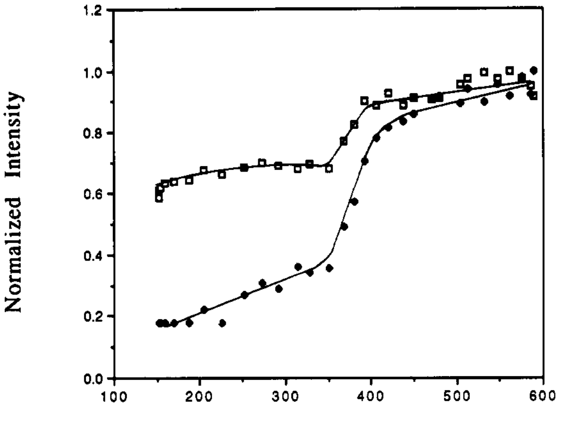

Figure 9. Ethane (□) and GaH (◆, mass 70) signals from 4 as a function of the pyrolysis furnace temperature.

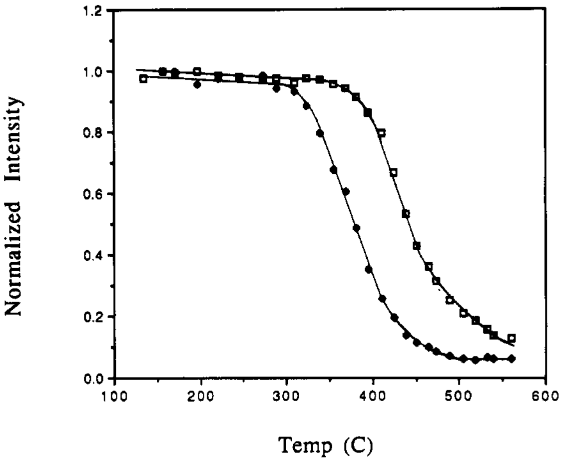

Figure 10. Isopropyl ligand (□) signal from 1 and *tert*-butyl ligand (◆) signal from 3 as functions of the pyrolysis furnace temperature.

matographic analysis, indicated both ethane and ethene were produced. Ethane has a weak unique peak in the mass spectrometer, and Figure 9 indicates that ethane formation began at temperatures as low as 350 °C. The other product, ethene, would result from a β-H elimination reaction and should result in the appearance of Ga–H signals. Figure 9 also shows that m/e signal for GaH began to increase at 350 °C. These species or As–H species provided the necessary H for ethane or isobutane formation. Note that the ethyl ligands of 4 began to be eliminated 75 °C lower than the methyl ligands of 3. This can be attributed to the low-energy β-H elimination pathway that was available to the ethyl ligands but not the methyl ligands.

Figure 10 demonstrates that elimination of the *t*-Bu ligands of 3 (and 4) occurred about 50–70 °C lower than elimination of the *i*-Pr ligands of 1, even though the mechanisms appear to be identical. This is consistent with a β-H elimination pathway since *t*-Bu ligands have three more β-H atoms than the *i*-Pr ligands and should therefore be more a reactive ligand. A similar activity trend exists in the activation energies for the β-H elimination reactions of *i*-PrI and *t*-BuI.[13] However, the higher reactivity of the *t*-Bu ligand is also consistent with homolytic fission reactions since the activation energy of *t*-Bu radical formation should be lower than that of *i*-Pr radical formation due to its increased stability.[14]

Discussion

Single-source organometallic semiconductor precursors must meet certain criteria in order to be valid alternatives to more conventional sources. Like any source, the compounds must be stable enough prior to and during sublimation that they can be reproducibly delivered. The unique 1:1 stoichiometry of the group-13 and -15 elements that the single-source precursors possess, however, imposes additional requirements on the compounds. First, low-temperature growth is required. Second, the reactivity of the ligands on the group-15 element must be such that the group-15 element can incorporate into a growing film at least as fast as the group-13 element is made available for film incorporation following its ligand loss. The decomposition studies presented here provide insight into precursor stability and reactivity that is necessary to evaluate precursors 1–4.

The dimeric precursors, 3 and 4, appeared to retain a 1:1 stoichiometry under the conditions of the studies reported here. Figure 5 demonstrated this by the parallel response of the Ga signal and the *t*-Bu ligand that was chemically bonded to As. The trimeric precursors, 1 and 2, were found to form diarsines during storage at room temperature over the period of several weeks. Diarsine formation from 1 was also observed to occur at or below the sublimation temperature 150 °C (Figure 2). The most graphic illustration of diarsine formation can be found in Figure 3, where the onset of tetramethyldiarsine formation from compound 2 can be observed at 125 °C for a sublimation temperature of 75 °C. Clearly compounds that lose the 1:1 stoichiometry by rearranging to give diarsines are unable to meet the requirement of reproducible delivery. The overall Ga:As ratio being delivered from a saturator containing a mixture of unconverted precursor (such as 1), diarsine, and the additional rearrangement products will vary with time due to volatility differences of the species present.

Diarsines are stable molecules that have been reported in the literature.[15] One possible reason the trimers formed diarsines and the dimers did not could be related not to the diarsine product but rather to the other product(s) that needs to form during precursor rearrangement. A stable product is necessary for diarsine formation. Two dialkylgallium radicals would result if dimers 3 or 4 rearranged to give tetra-*tert*-butyldiarsine. The compound $[(\mathrm{thf})\mathrm{Br_2Ga}]_3\mathrm{As}$ has been reported in the literature.[16] This trigallium arsenic compound forms the basis for suggesting a related compound, $[\mathrm{Me_2Ga}]_3\mathrm{As}$ for example, may have formed during rearrangement of 1 and 2 to the diarsines. We were unable to detect $[\mathrm{Me_2Ga}]_3\mathrm{As}$; however, the suggestion of such a compound is at least consistent with our observations.

Ligand removal from 3 and 4 is discussed below because these precursors did not undergo low-temperature reactions in their saturators. The appearance of isobutene, isobutane (propene and propane for 1), and ethane is consistent with β-H elimination and intramolecular hydride–alkyl ligand coupling reactions for alkyl ligands containing β-H functionality, such as *t*-Bu, *i*-Pr, and ethyl. Our data do not establish the ligand decomposition

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[13] Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: New York, 1976.

[14] Streitwieser, A.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillian: New York, 1981.

[15] Cullen, W. R. *Adv. Organomet. Chem.* **1966**, *4*, 145.

[16] Wells, R. L.; Safieezad, S.; McPhail, A. T.; Pitt, C. G. *J. Chem. Soc., Chem. Commun.* **1987**, 1823.

pathways and homolytic decomposition followed by radical abstraction reactions are possible but unlikely because of the low pressures employed (1×10^{-2} Torr). In either case, the temperatures of ligand loss rather than the detailed reaction pathways are more relevant to identifying conditions under which single-source precursors should lead to film growth. The detailed surface reactions are under investigation and likely influence the quality of the film and the incorporation of carbon impurities.

One of the challenges for GaAs is to realize film growth at low temperatures. Single-source precursors require low-temperature growth to prevent the preferential evaporation of As from the film. Low-temperature growth would also minimize dopant diffusion and diffusion across heterojunctions. A growth temperature of 500 °C, which is well below the congruent sublimation temperature of GaAs (ca. 640 °C),[17] has been our design target for the GaAs single-source precursors. As described in the Experimental Section, the extent of conversion of a ligand, at a specific temperature, is a function of the residence time of the precursor in the heated zone. At sufficiently long residence times in a heated zone the ligand should be completely reacted as long the process is irreversible. Therefore differences in residence times must be accounted for when interpreting the results of this study in terms of film growth. However, the short residence times realized in this study should be similar to those occurring in the CBE system in which we deposited GaAs films. With this in mind, the results indicate that low-temperature growth is indeed a possibility. Compounds **3** and **4** contain *t*-Bu ligands that began to react at 325 °C (Figures 7 and 8) regardless of the ligands on Ga (ethyl or methyl). The onset of methyl ligand removal from **3** was 425 °C (Figure 7) and the ethyl ligands of **4** appeared to begin reacting at 350 °C (Figure 9), suggesting that film growth should be possible at temperatures as low as 425 °C for **3** and at least as low as 350 °C for **4**.

A final, but not necessarily sufficient, criterion for a single-source precursor is that the portion of the precursor that contains the group-15 element must decompose and be incorporated into the film at least as readily as the portion that contains the group-13 element. This is because excess group-13 material will remain on the surface as droplets and degrade the crystal quality. In extreme cases, whisker growth from the surface results. Any excess group-15 material, however, will not remain on the surface.[18] For this reason, the most promising precursor may be **3** since the *t*-Bu ligands of the As atoms can clearly be seen to react at lower temperatures than the methyl groups of the Ga atoms. Films grown in CBE systems utilizing Me_3Ga as a source, however, have been universally plagued by high carbon levels.[19] The β-H elimination reaction of the *t*-Bu groups may reduce carbon incorporation in this case by providing H to react with the methyl groups. Carbon incorporation should not be an issue for **4**. The β-H elimination reaction of the ethyl ligands provides a clear mechanism to reduce carbon levels. However, unlike the reactivities of the methyl and *t*-Bu ligands, the reactivities of the ethyl and *t*-Bu ligands are very similar. This may lead to an excess of gallium being deposited at low temperatures. At higher temperatures where both reactions rapidly go to completion this is less likely to be a problem.

In a following paper[20] we report the use of compounds **3** and **4** to grow epitaxial and polycrystalline films on (100) GaAs substrates. Consistent GaAs film growth from compound **1** was not possible. At sufficiently low reactor pressures (5×10^{-6} Torr), the type of film, epitaxial versus polycrystalline, was temperature dependent. Epitaxial films were grown from **3** at 475–550 °C and polycrystalline films were grown at 425–450 °C. At temperatures below 425 °C GaAs films could not be obtained from **3**. For compound **4**, epitaxial films were observed at 400–525 °C. At higher reactor pressures only polycrystalline films were obtained, with whiskers growing from the surface in one case.

The decomposition studies reported here provide the insight into precursor stability and reactivity that is needed to explain the film growth results. The inability to grow GaAs films reproducibly from **1** is consistent with formation of diarsines and loss of precursor stoichiometry. In addition, the temperature at which we observed the onset of methyl ligand removal from **3** was also the lowest temperature at which we were able to deposit GaAs films from compound **3**. Furthermore, the growth rates observed for **3** and **4** correlate with the extent of reaction observed for the ligands on the Ga atoms.[20] This is expected since, as discussed above, excess As will desorb but Ga will not. Also, this correlation demonstrates the validity of the earlier assumption that the residence time of precursors in the heated zone of the pyrolysis apparatus is similar to that of precursors reacting in our CBE apparatus. This suggests that polycrystalline films obtained from **3** at 425 and 450 °C may have resulted from incomplete reactions of Ga–Me species on the growing surface. At 475 °C where epitaxial films were obtained the pyrolysis results indicate that methyl ligand removal was essentially complete (Figure 7). The observation that the films became polycrystalline as the reactor pressure was raised is an indication that gas phase reactions adversely affect film growth from single-source precursors. Since whisker growth is an indication of excess Ga on the surface, gas-phase reactions appear to affect the Ga:As ratio being delivered to the surface.

The pyrolysis studies, in conjunction with the film growth studies, lead to the conclusion that epitaxial GaAs film growth can be achieved from properly designed single-source precursors. The criteria of low-temperature stability was met for the dimeric precursors **3** and **4** but not by the trimeric precursors **1** and **2**, which formed diarsines. The temperature requirements were also met by the dimeric precursors. However, epitaxial growth was realized only when the precursor molecule was delivered intact to a substrate that was at a sufficiently high temperature for ligand loss from both the Ga and As moieties to proceed.

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Registry No. 1, 133671-00-8; 2, 12154-44-8; 3, 106417-80-5; 4, 138834-30-7; GaMe, 99601-83-9; GaH, 13572-92-4; GaAs, 1303-00-0; tetramethyldiarsine, 471-35-2; triisopropylarsine, 57538-64-4; tetraisopropyldiarsine, 138783-31-0; trimethylarsine, 593-88-4; 2,3-dimethylbutane, 79-29-8; isobutene, 115-11-7; isobutane, 75-28-5.

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