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Chemical Beam Epitaxy and Characterization of GaAs from Bis(*tert*-butylarsenido)dimethylgallane Dimer and Bis(*tert*-butylarsenido)diethylgallane Dimer

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The effects of reactor pressure and film growth temperature on growth rates and film properties were investigated for chemical beam epitaxy of GaAs from the single-source precursors bis(*tert*-butylarsenido)dimethylgallane dimer, $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$, and bis(*tert*-butylarsenido)diethylgallane dimer, $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$. Single-crystal epitaxial films could only be obtained at low reactor pressures (5×10^{-6} Torr). Epitaxial layers, which were highly doped with carbon acceptors (10^{18}–10^{19} cm^{-3}), were deposited from $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ at temperatures of 475–550 °C. Polycrystalline films were obtained at lower temperatures, and film growth was not possible below 423 °C. Epitaxial films were obtained from $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ over the temperature range 400–525 °C. The films deposited from $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ were inhomogeneous and also contained high levels of carbon (5×10^{18}–3×10^{19} cm^{-3}). Growth rates and film properties were found to be directly related to reactions of the Ga–Me ligands for $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ and the Ga–Et ligands for $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$. A model is suggested to explain the results in which a self-limiting mechanism exists for the deposition of Ga atoms from $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ but not from $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$.

Introduction

In a recent communication[1] we reported the growth of epitaxial films from bis(*tert*-butylarsenido)dimethylgallane dimer, $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$, under chemical beam epitaxy (CBE) conditions. We present here a complete discussion of the use of single-source precursors for GaAs that have the general formula $[R_2Ga(\mu\text{-AsR}'_2)]_2$ and lead to epitaxial films. The effect of reactor pressure as well as the temperature dependence of growth rates and film properties were investigated for CBE growth of GaAs from the single-source precursors $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ and bis(*tert*-butylarsenido)diethylgallane dimer, $[Et_2Ga(\mu\text{-As-}tert\text{-Bu}_2)]_2$. The film properties and growth rates discussed below are related to the decomposition pathways of the precursors, which were presented in an earlier paper.[2]

In CBE growth of GaAs using conventional precursors, the growth rates and film properties such as carrier concentration have shown significant dependence on the temperature of growth and on the choice of the Ga precursor. Several groups have investigated CBE growth of GaAs using trimethylgallium (Me_3Ga) and triethylgallium (Et_3Ga) with both arsine and solid arsenic sources.[3] The films obtained in those studies were generally p-type due to the incorporation of carbon. Those films grown with Me_3Ga typically contained greater than 1×10^{19} carbon atoms/cm^3, whereas films grown from Et_3Ga contained 1×10^{14}–1×10^{16} carbon atoms/cm^3. The decrease in carbon incorporation for Et_3Ga likely stems from the β-H elimination reaction available to the ethyl ligands. Similar results were expected for the methyl- and ethyl-based precursors used in this work.

Experimental Section

GaAs thin films were grown from $[Me_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ and $[Et_2Ga(\mu\text{-As-}t\text{-Bu}_2)]_2$ in the CBE system previously described.[1] The films were deposited on undoped, semiinsulating (100) GaAs substrates (Litton, Airtron Division). The wafers were ultrasonically solvent cleaned, etched with an 8:1:1 H_2SO_4:H_2O:H_2O_2 solution, and loaded into the preparation chamber of the reactor, where they were pretreated in H_2 to react away the oxides.[1]

The organometallic precursors used in this study had been purified by recrystallization from dichloromethane, and the resulting material was analyzed for impurities. The most significant contaminant was found to be silicon. Graphite furnace atomic absorption spectroscopy indicated a Si concentration of 200 ppm. The high Si content of the sources was not entirely unexpected since silicone grease has been used on some of the joints of the synthesis glassware. Future synthetic efforts will avoid the use of silicone grease.

The effect of reactor pressure on film quality was investigated by depositing films from the precursors at pressures of 1×10^{-4}, 1×10^{-5}, 5×10^{-6}, and 1×10^{-6} Torr while keeping the other parameters constant. The resulting films were analyzed by X-ray diffraction. The reactor pressure was manipulated by adjusting the flow rate of H_2 carrier gas through the saturator containing the organometallic compound. Calibrations indicated that adjusting the pressure from 5×10^{-6} to 1×10^{-4} Torr resulted in ca. 3 times more precursor being delivered to the reactor. This was reflected by a comparable increase in growth rate. Increasing the pressure also had the effect of diluting the precursor from ca. 30 mol % at 5×10^{-6} Torr to only a few percent at 1×10^{-4} Torr,[4] suggesting that at the higher flow rates the sublimation rate of the compound was insufficient to fully saturate the flowing gas.

Growth rates for the two precursors were studied as a function of substrate temperature. The growth rates were determined by masking part of a substrate with a flat tantalum wire, depositing a film, and measuring the height of the resulting step with a profilometer. During these studies, the reactor pressure was

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(1) Miller, J. E.; Ekerdt, J. G. *Chem. Mater.* **1992**, *4*, 7.

(2) Miller, J. E.; Mardones, M. A.; Nail, J. W.; Cowley, A. H.; Jones, R. A.; Ekerdt, J. G. *Chem. Mater.* **1992**, *4*, 447.

(3) See: Tsang, W. T. *J. Cryst. Growth* **1990**, *105*, 1. Davies, G. J.; Andrews, D. A. *Chemtronics* **1988**, *3*, 3 and references therin.

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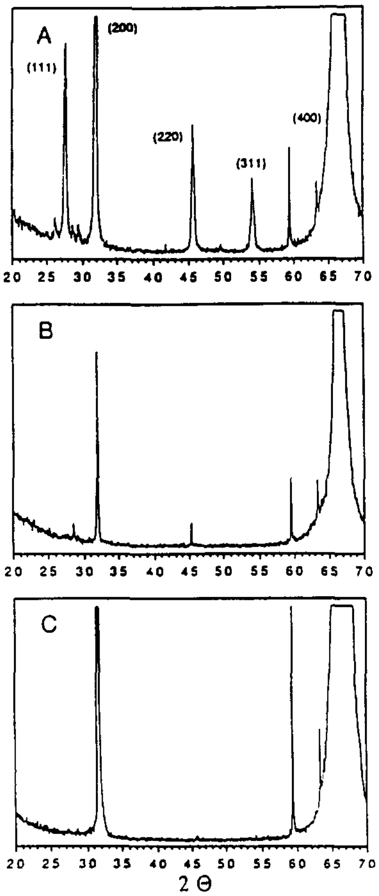

Figure 1. Single-crystal X-ray diffraction patterns of films grown from $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ on (100) GaAs substrates at 525 °C and (A) 1×10^{-4} Torr, (B) 1×10^{-5} Torr, and (C) 1×10^{-6} Torr.

maintained at 5×10^{-6} Torr and the oven containing the organometallic source was regulated at 135 °C for $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ and 150 °C for $[Et_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$. Experience had shown these temperatures to give similar growth rates. The substrate temperature was varied between 400 and 550 °C in 25 °C intervals for growth from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$. For growth from $[Et_2(Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$, the substrate temperature was varied between 400 and 525 °C in 25 °C intervals. A film was not grown at 550 °C from $[Et_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ because the lower thermal stability of this compound[2] led to problems with deposits obscuring the viewport used to transmit IR radiation for substrate heating. The relatively rapid formation of these deposits decreased the transparency of the viewport significantly enough during a single 10-h deposition that 525 °C was the highest temperature that could be maintained throughout the run.

The effect of growth temperature on the film properties was also examined. A series of films was grown at different temperatures from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ and $[Et_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ and subsequently examined by X-ray diffraction, scanning electron microscopy (SEM), Hall effect, and secondary ion mass spectrometry (SIMS). A third precursor, $[Me_2Ga(\mu\text{-}As\text{-}i\text{-}Pr_2)]_3$, was studied briefly but rejected because it could not be reproducibly delivered to the reactor, presumably due to the low-temperature reactions discussed in ref 2, which result in diarsine formation. The depositions were carried out under the same conditions used in the growth rate studies, and the thicknesses of the resulting films were inferred from the growth rate studies and deposition times (10 h for each film).

Results

The key to obtaining epitaxial films from single-source precursors such as $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ appears to lie in low operating pressures. The effect of pressure is well illustrated in Figure 1 for films grown at 525 °C from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$. Figure 1A is the X-ray diffraction pattern (Cu Kα radiation) obtained from a 3-μm-thick GaAs film deposited on a (100) GaAs substrate at a reactor pressure of 1×10^{-4} Torr. The 400 and 200 reflections of the substrate are clearly present at 66.4° and 31.9°, respectively. However 111, 220, and 311 reflections are also present at 27.4°, 45.6°, and 54.0°, respectively, indicating that the GaAs overlayer is polycrystalline. The two additional peaks in the pattern located at 2θ values of 59.2° and 63.2° are the 400 reflections of Cu Kβ and W Lα radiation, respectively.[5] Figure 1B is the X-ray diffraction pattern of a 1.2-μm-thick GaAs film deposited at a pressure of 1×10^{-5} Torr. Note that the only evidence of polycrystallinity is the very weak 220 reflection, demonstrating the improved nature of the film. The very weak peak at a 2θ of 28.6° is the 200 Cu Kβ reflection. Figure 1C shows the X-ray diffraction pattern of a 0.6-μm-thick film deposited at 1×10^{-6} Torr. Only 200 and 400 reflections are present, indicating the epitaxial nature of the deposit. Although some of the changes in Figure 1 may have resulted from differing thicknesses of the specific films shown, the illustrated trend is representative of a large number of films of varying thickness grown at a variety of temperatures and pressures.

The surfaces of the films deposited at 1×10^{-4} Torr generally appeared hazy. The surfaces of those deposited at 1×10^{-5} Torr showed improvement, but each exhibited a few small hazy patches. SEM analysis of the films revealed the haziness to result from small crystallites ca. 1 μm in size. Mirrorlike, epitaxial films, which appeared featureless to the SEM (features < 1 μm), were only obtained by operating the reactor at pressures of 5×10^{-6} Torr and below.

Due to the positive effect of reduced pressure on film quality, experiments were undertaken to better characterize the growth pressure.[4] This was necessary because the ionization gauge used to measure the reactor pressure was located near the inlet to the turbomolecular pump, a position remote from the substrate. Space limitations prevented the pressure over the substrate from being directly measured. Therefore pressures were measured in the line upstream from the doser and in the reaction chamber downstream from the doser. This allowed upper and lower limits to be set on the actual pressure above the substrate surface. The experiments revealed that the pressure in the doser inlet line was as much as 3 orders of magnitude higher than that indicated by the ionization gauge; however, pressures measured in the reaction chamber were only 3–5 times higher than the ionization gauge pressure reading. Thus for an operating pressure of 1×10^{-4} Torr, the pressure changed from 2×10^{-1} to 6×10^{-4} Torr between the saturator and the substrate surface. For an operating pressure of 1×10^{-5} Torr, the pressure changed from 1.5×10^{-2} to 5×10^{-5} Torr, and for an operating pressure of 5×10^{-6} Torr the pressure changed from 5×10^{-3} to 2×10^{-5} Torr. Therefore it is impossible to rule out gas-phase reactions as being the cause of the poor film quality obtained at the higher operating pressures.

The results from the growth rate studies are shown in Figure 2. Roughening of the surfaces near the edge of the tantalum masks coupled with the fact that the masks did

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[5] The Kβ line from the Cu X-ray source was not fully removed by the nickel filter. The W-Lα line arose from W metal which had been deposited on the Cu target by the filament in the X-ray tube.

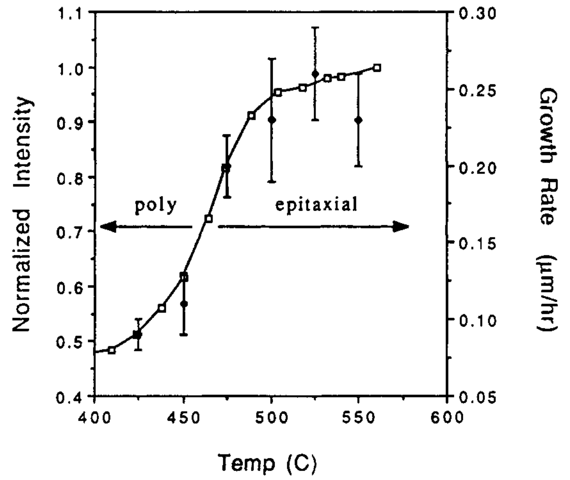

Figure 2. Temperature dependence of the GaAs growth rate from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ (♦). The temperature dependence of methane formation from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ in pyrolysis studies[2] is shown for comparison (□).

not produce abrupt steps resulted in some uncertainty in the step heights. This is reflected by the error bars in the figure. The figure reveals that the growth rate for $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ was a constant for temperatures of 500 °C and above and temperature dependent below 500 °C. At 400 °C GaAs could not be deposited from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$. The figure also illustrates the similarity between the temperature dependence of the growth rate and the temperature dependence of methane formation from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ during separate pyrolysis studies.[2]

Single-crystal X-ray diffraction analysis of the films obtained from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ revealed that polycrystalline layers were grown at 425 and 450 °C. Crystallites of ca. 1 µm in size were observed during SEM analysis of the films deposited at 425 and 450 °C. To the eye, these films exhibited a barely perceptible cloudiness. At 400 °C a black, nonuniform deposit was obtained that XPS analysis revealed to be made up of as much as 40% carbon. Epitaxial films were grown over the temperature range 475–550 °C. Each of the epitaxial films grown from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ had a mirrorlike appearance with the exception of a hazy area on the film deposited at 550 °C. The epitaxial films appeared featureless under SEM analysis (features < 1 µm). X-ray analysis of the same films with a system utilizing a four-crystal monochromator revealed that the film grown at 475 °C was mismatched to the substrate (Figure 3).

The net carrier concentrations and Hall mobilities at room temperature of the epitaxial films grown from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ are given in Table 1. The films were all p-type and highly doped. SIMS analysis with oxygen sputtering to enhance the yield of secondary ions indicated that carbon and silicon were the primary impurities, as expected. Bulk carbon levels are given in Table 1. The silicon content of typical films grown from both precursors was $(2\text{–}4) \times 10^{18}$ cm^{-3}. Enhanced carbon and silicon signals were observed in the first 300–400 Å of the surface. Although it is possible that there was some contamination near the surface due to the instrument, it is not usual for it to appear to the extent seen for these samples. The enhanced SIMS yields could have resulted from surface roughness caused by islands or particles that were less than 1 µm in size and therefore unobservable in the SEM.

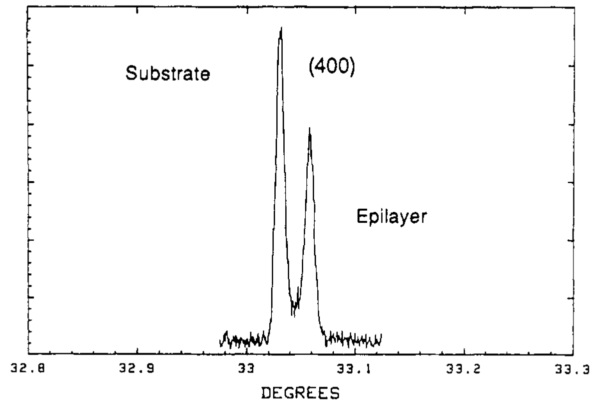

Figure 3. Five-crystal X-ray diffraction pattern obtained from a film deposited from $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ on (100) GaAs at 475 °C and 5×10^{-6} Torr showing mismatch between the film and substrate.

Table 1. Room-Temperature Hall Mobilities, Net Carrier Concentrations and Bulk Carbon Concentrations Determined by SIMS for *p*-Type Films Deposited from $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$

deposition temp (°C)	thickness (µm)	μ_H (cm^2/V s)	N_a (cm^{-3})	carbon (cm^{-3})
425	0.9		polycrystalline	
450	1.1		polycrystalline	
475	2.0	54	5.0×10^{19}	
500	2.3	58	1.1×10^{19}	1×10^{19}
525	2.3	66	7.3×10^{18}	2×10^{19}
550	2.3	94	1.6×10^{18}	6×10^{18}

The Hall results indicate that the carrier concentration decreased as the growth temperature increased. Similar behavior has been observed for CBE growth of GaAs utilizing Me_3Ga and a solid As source.[6,7] The mobilities of the films were slightly lower than the values expected for the carrier concentrations suggesting some degree of compensation. This is corroborated by the fact that the carbon level measured by SIMS was larger than the concentration given by the Hall data.

Figure 4 shows that the growth rate for $[Et_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ was constant throughout the temperature range 400–525 °C. In addition, the figure demonstrates that the temperature dependence of the growth rate was similar to the temperature dependence of reactions in the pyrolysis studies involving the ethyl ligands of the precursor as evidenced by the appearance of Ga–H species. These species probably arose from β-H elimination of ethyl groups.[2] Furthermore, the figure shows that the growth rate appeared to be unaffected by the fact that the *tert*-butyl ligands were less reactive than the ethyl ligands at lower temperatures (400–450 °C).

X-ray analysis of the films deposited from $[Et_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ indicated that epitaxial films were obtained throughout the temperature range 400–525 °C. No mismatch with the substrate was observed for any of the layers with the four-crystal X-ray diffraction system. The surface of each of the films grown in the temperature range 400–475 °C exhibited a barely perceptible haziness. The films grown in the temperature range 500–525 °C were generally mirrorlike with a few clouded areas. However,

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(6) Konagai, M.; Yamada, T.; Akatsuka, T.; Saito, T.; Tokumitsu, E.; Takahashi, K. *J. Cryst. Growth* **1989**, *98*, 167.

(7) Konagai, M.; Yamada, T.; Akatsuka, T.; Nozaki, R.; Miyake, K.; Saito, T.; Fukamachi, T.; Tokumitsu, E.; Takahashi, K. *J. Cryst. Growth* **1990**, *105*, 359.

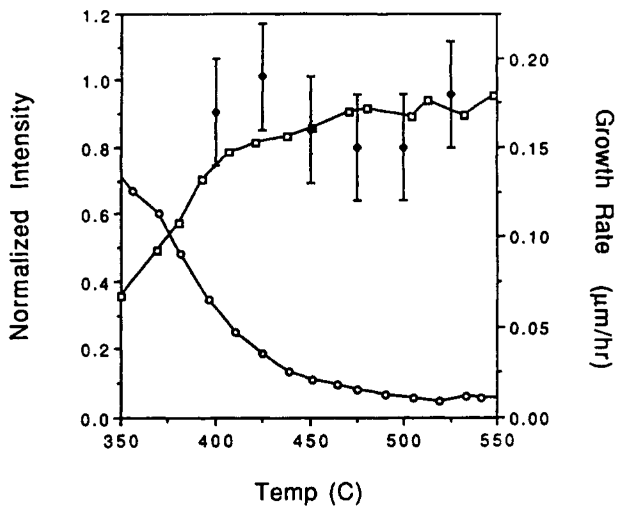

Figure 4. Temperature dependence of the GaAs growth rate from $[Et_2Ga(\mu\text{-As-}tert\text{-}Bu_2)]_2$ (◆). Temperature dependence of the Ga-H (□) and *tert*-butyl ligand (○) signals from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ in pyrolysis studies[2] are shown for comparison.

Table 2. Room-Temperature Hall Mobilities and Net Carrier Concentrations, and Bulk Carbon Concentrations Determined by SIMS for *p*-Type Films Deposited from $[Et_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$

deposition temp (°C)	thickness (µm)	μ_H (cm²/V s)	N_s (cm⁻³)	carbon (cm⁻³)
400	1.8	42	5.3×10^{19}	3×10^{19}
425	1.8	39	5.1×10^{19}	
450	1.8	37	3.1×10^{19}	3×10^{19}
475	1.8	13	1.8×10^{19}	
500	1.8	26	6.5×10^{17}	5×10^{18}
525	1.8	45	1.3×10^{18}	5×10^{18}

SEM analysis revealed no surface features of greater than 1 µm in size for any of the films.

The room temperature net carrier concentrations and mobilities given by the Hall measurements for the films grown from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ are presented in Table 2. Carbon levels determined by SIMS are also given in Table 2. Enhanced yields of carbon and silicon were again observed in the first 400 Å of the surface.

Discussion

The effect of reactor pressure on the quality of films is not well understood. However, in an earlier version of the deposition system, whisker growth was occasionally observed when operating at a pressure of 1×10^{-4} Torr, suggesting that higher pressures lead to excess Ga accumulating on the growing surface. However, the fact that whisker growth can occur simultaneously with epitaxial film growth[8] suggests other effects are also present. These effects are likely related to the Ga–As bond of the precursor since conventional GaAs precursors do not significantly suffer from this problem even though they are commonly used at much higher partial and total pressures.

The results from the growth rate experiments indicate that the Ga–alkyl ligands of the precursors controlled both the growth rate and the film properties. For example, the similarity between the temperature dependence of the growth rate and methane formation from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ (Figure 2) suggests that at temperatures below 500 °C the growth rate was kinetically limited by loss of methyl ligands from the Ga atoms of the precursor. Likewise, Figure 4 shows that the temperature dependence of the growth rate from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ is similar to the temperature dependence of reactions involving the ethyl ligand of the Ga, not the *tert*-butyl ligands of the As.

The most readily observable effect of the Ga–alkyl ligands on the film properties is the crystallinity. Comparing the data for the growth rate and pyrolysis of $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ presented in Figure 2 to the crystallinity of the films suggests that film quality was directly related to the reactions involving the methyl ligand of the precursor. Note that the temperature at which the onset of methyl ligand removal was observed during pyrolysis, 425 °C, was also the lowest temperature at which GaAs films could be deposited from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$. Recall that at 400 °C a carbonaceous deposit was obtained. This suggests that the polycrystalline films obtained at 425 and 450 °C resulted from incomplete reactions of Ga–Me species on the growing surface. At 475 °C, where the pyrolysis results indicated that methyl ligand removal was nearly complete, a mismatched epitaxial layer was obtained that could be due to a high level of carbon incorporation.[6] Indeed, the carbon level calculated by Vegard's law corresponding to the observed lattice parameter of the film is 4×10^{19} cm⁻³, a value similar to the net hole concentration given by Hall measurements. Finally, at higher temperatures where the pyrolysis results indicate that the methyl ligands were fully removed, lattice matched epitaxial layers were obtained.

Figure 4 shows that the ethyl ligands of $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ were slightly more reactive than the *tert*-butyl ligands at the lowest growth temperatures. Despite the reduced reactivity of the *tert*-butyl ligands, lattice matched epitaxial layers were grown throughout the temperature range investigated. When compared to the results for $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ where incomplete reactions resulted in polycrystalline films, this result suggests that the reaction of the ethyl ligand and not the *tert*-butyl ligand was primarily responsible for determining the crystallinity of the film.

The effect of the Ga–alkyl ligands on film properties other than crystallinity is less obvious. The decrease in carriers and increased mobility in the films grown from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ with increasing temperature likely stems from a continuation of the trend discussed above in which higher temperatures more efficiently remove methyl ligands from the Ga atoms.

The improvement in quality expected for films deposited from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ over those deposited from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2$ due to the β-H elimination mechanism available to the ethyl ligands was not realized. On the contrary, films deposited from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ exhibited high carrier concentrations and low mobilities (Table 2). The films were all p-type and contained high levels of carbon. Furthermore, the films seemed to be inhomogeneous since the mobilities did not correlate with either the SIMS results or the carrier concentrations. For the films grown at temperatures less than 475 °C, high carbon concentrations may have resulted from incomplete loss of *tert*-butyl ligands (Figure 4). Since the films deposited from $[Me_2(Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ were homogeneous in at least two dimensions and the ligands on the As atoms were identical for both precursors, the ethyl ligands of $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ are implicated as the origin of the inhomogeneities.

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[8] Kasahara, J.; Kajiwara, K.; Yamada, T. *J. Cryst. Growth* 1977, *38*, 23.

The results for $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ are inconsistent with what has been observed for CBE growth of GaAs using Et_3Ga as a source. The carrier concentrations typically realized for CBE are less than 1×10^{16} cm^{-3}.[3] Carrier concentrations greater than 1×10^{19} cm^{-3} were given by Hall measurements for the four samples grown at the lowest temperatures in this study. Furthermore, the carrier concentration from carbon incorporation typically increases with growth temperature for CBE growth of GaAs from Et_3Ga presumably due to increased cracking of the ethyl ligands at higher temperatures.[9] The trend appeared to be the opposite in this study. In addition, the mobilities were not only lower than expected but seem to be unrelated to the carrier concentration. This behavior may have resulted from sample inhomogeneities,[10] although compensation effects may have also played a role.

Below we suggest a model to explain these results based on the reactivities of the Ga ligands and the relative binding energies of Ga and As atoms on GaAs surfaces. Consider growth from a single molecule of an arbitrary single-source precursor of 1:1 Ga:As stoichiometry on a perfect GaAs crystal. If the Ga–As bonds of the precursor dissociate on the growth surface, several possibilities exist: (1) The simplest result is that both the Ga and the As moieties desorb leaving an unchanged stoichiometric crystal. (2) The next possibility is that both the Ga and As moieties react (i.e., the ligands are eliminated) and the Ga and As are incorporated into the crystal as stoichiometric GaAs. (3) Another possibility is that the Ga species desorb and the As species react. This would result in a surface with excess As. However the vapor pressure of As at typical growth temperatures is such that the excess As atoms would desorb from the GaAs surface,[11] which again would leave stoichiometric GaAs. (4) Finally, if the As species desorb and the Ga species react, then the result is a surface with excess Ga. Under typical growth conditions excess Ga will not desorb.[11] Thus this final process would result in nonstoichiometric growth. We suggest that the second possibility is responsible for film growth but that the elimination reactions of the Ga–alkyls must be limited to prevent the fourth possibility. Such a limitation exists for Ga–Me moieties, but not for Ga–Et moieties. Ga–Me is less reactive than Ga–Et;[2] therefore, it is less likely that Ga–Me will lead to free Ga atoms on the surface.

Differences between Ga–Me and Ga–Et ligand reactivities have been observed with more conventional CBE precursors. It has been reported that very little Me_3Ga can be decomposed on GaAs surfaces under CBE conditions without the presence of adsorbed As.[6,7,12-14] In fact, excess Me_3Ga has intentionally been used in CBE growth of GaAs because As-rich conditions resulted in poor surface morphologies.[6] The same is not true of Et_3Ga; under Ga-rich conditions Ga droplets can readily be deposited.[12] The implication is that during CBE, the methyl-based chemistry is inherently self-limiting, whereas the ethyl-based chemistry is not. Surface science studies aimed at determining the mechanism of atomic layer epitaxy suggest that the self-limiting nature of the methyl-based chemistry might be due to adsorbate inhibition.[15] That is, methyl groups on the surface inhibit further decomposition of Me_3Ga. This model is supported by kinetic data, which show that methyl groups desorb around 10 times faster from As-rich GaAs surfaces than from Ga-rich surfaces.[16] Evidence also exists to support a flux balance model that states Me_3Ga may decompose on a Ga rich surface, but Ga-containing species desorb at the same rate of decomposition so that no net Ga deposition occurs.[17,18]

The results obtained in our study are easily explained by the model of self-limited growth. For deposition from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$, the growth rate was limited by elimination of the methyl groups. This was expected since the decomposition studies[2] indicated that the *tert*-butyl groups of the $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ were more reactive than the methyl groups and were eliminated at lower temperatures. At higher temperatures (>500 °C) where reactions of both the methyl and *tert*-butyl ligands were essentially complete in pyrolysis studies,[2] desorption of some As atoms from the surface may have occurred. However, Ga–Me species which then accumulated on the surface may have prevented the deposition of a large excess of Ga through an adsorbate inhibition type process. Furthermore, Ga–Me can desorb from GaAs (100) at temperatures as low as 300 °C following dissociation of the Ga–As bond of the precursor.[19] This desorption possibility provides another means to prevent excess Ga forming from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$. As has been demonstrated the self-limiting mechanism for Ga–Me species exists for only a limited time, i.e., the methyl groups will eventually be lost from Ga atoms even in the absence of As, especially at higher temperatures.[20] Thus the hazy patches on the film grown from $[Me_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ at 550 °C probably resulted from a partial breakdown of the self-limiting mechanism.

For deposition from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$, the growth rate also appeared to be controlled by elimination of the ethyl groups despite the fact that the ethyl groups of $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ were shown to be slightly more reactive than the *tert*-butyl groups (Figure 4) in the decomposition studies.[2] The poor film quality resulted because Ga atoms were produced by the Ga–Et species in the absence of sufficient As atoms to produce stoichiometric GaAs. The lack of stoichiometry then resulted in the formation of defects and inhomogeneities, possibly through a mechanism in which excess Ga atoms coalesced to form islands. Recall that the films grown from $[Et_2Ga(\mu\text{-As-}t\text{-}Bu_2)]_2$ in the temperature range 400–475 °C, where excess Ga formation was most likely, appeared hazy and contained the highest carbon levels. However, the model and the results indicate that even under conditions that result in the complete elimination of ligands from the As atoms, As desorption can result in a build up of excess Ga atoms on

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the surface when no self-limiting mechanism exists for the Ga ligands.

What is required of a single-source GaAs precursor therefore appears to be a self-limiting reaction process to prevent the accumulation of Ga on the growth surface. The precursor $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ appears to have such a process, but unfortunately high levels of carbon incorporation limit its usefulness. Furthermore, the self-limiting process may break down at higher temperatures for this precursor. A solution may lie in the use of single-source precursors that employ Ga:As ratios other than 1:1. This is essentially the approach used in MOCVD when the group V source is supplied in excess. Examples of single-source precursors with a V/III ratio of greater than one include tris(di-*tert*-butylarsino)gallane, ($Ga(As\text{-}t\text{-}Bu_2)_3$), tris(di-*tert*-butylphosphino)gallane, $Ga(P\text{-}t\text{-}Bu_2)_3$, tris(di-*tert*-butylphosphino)indane, $In(P\text{-}t\text{-}Bu_2)_3$,[21] and tris(di-*tert*-butylarsino)alane, $Al(As\text{-}t\text{-}Bu_2)_3$.[22] The feasibility of this alternate approach is currently being studied in our laboratory.[19,23]

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