



Ligand exchange reactions in InGaAs metalorganic vapor-phase epitaxy

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Abstract

Metalorganic vapor-phase epitaxy of $\text{In}_y\text{Ga}_{1-y}\text{As}$ from triethylgallium, trimethylindium and tertiarybutylarsine was studied using on-line infrared spectroscopy to monitor the organometallic compounds in the feed and effluent gases. The film composition was measured by X-ray diffraction. Ligand exchange reactions between the group III sources were found to occur in the feed lines. The new species produced were trimethylgallium, dimethylethylgallium, methyldiethylgallium, dimethylethylindium and methyldiethylindium. The thermal stability of these species varied over a wide temperature range. For example, the ethylindium compounds started to decompose at 250°C, while trimethylgallium began to react at 500°C. In the square-duct reactor used in this study, the wide variation in the reactivity of the precursors resulted in films that were indium rich near the reactor inlet and gallium rich near the reactor outlet. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fabrication of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ hetero-junction bipolar transistors (HBTs) requires accurate control of the indium content to within 0.1% in order to lattice match the InGaAs layer to the InP substrate and to obtain the highest electron mobilities. It is essential that the InGaAs layer is

highly uniform in composition, thickness and crystallinity, since slight variations in these properties will seriously degrade the quality of the InGaAs epilayer [1].

Low-temperature growth of InGaAs is of interest for manufacturing high-speed HBTs. Heavily p-type doped InGaAs base layers are fabricated by incorporating carbon into the film using CCl_4 at growth temperatures between 425°C and 500°C [2–4]. Higher temperatures are not effective at achieving high doping levels. Trimethylindium (TMIn) and trimethylgallium (TMGa) are typically

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used as sources for high-temperature InGaAs growth [5–7]. However, for low-temperature deposition, triethylgallium (TEGa) must be substituted for TMGa.

Ligand exchange reactions between trimethylamine alane and TMGa precursors were observed during AlGaAs MOVPE, leading to the growth of non-uniform layers [8]. Recently, we found that exchange reactions occur between diethylzinc and dimethylcadmium in the feed lines on the way to the reactor [9]. It can be expected that similar reactions occur during the growth of InGaAs using TEGa and TMIIn, which may lead to compositional non-uniformities in the film.

In this study, on-line infrared spectroscopy was used to monitor the gas composition of the reactor feed and effluent during MOVPE of InGaAs below 600°C. Ex situ X-ray diffraction was used to determine the InGaAs composition over the length of the film. It is shown that exchange reactions indeed take place between TEGa and TMIIn, resulting in the segregation of indium and gallium in the InGaAs layers.

2. Experimental methods

The InGaAs films were deposited on the glass walls of a low-pressure tube reactor at 99 Torr. Electronic-grade TMIIn, TEGa and TBAs were contained in stainless steel bubblers immersed in thermal regulating baths at 25°C, 20°C and 4°C, respectively. The precursors were vaporized into 3–280 cm³/min of hydrogen, then diluted with hydrogen to a total flow between 100 and 1200 cm³/min (NTP). The hydrogen was purified by diffusion through a palladium membrane. The tubular glass reactor and heater design have been described previously [10,11].

The organometallic compounds in the reactor feed and effluent were identified by infrared and mass spectroscopies (Leybold Inficon 300 amu mass spectrometer). Infrared spectra of the gas streams were collected on a BioRad FTS-7 infrared spectrometer by passing them through a small flow cell, 17.7 cm long by 3.0 cm in diameter, that was sealed with KBr windows. Peak heights of the characteristic metal–carbon stretches of each species

were used as a measure of concentration. The peak heights were related to the species concentration through the following calibration procedure. The concentrations of the sources were determined using mass spectrometry by measuring the hydrocarbons produced during complete pyrolysis of each organometallic compound at 650°C. The mass spectrometer signals were calibrated using hydrocarbon gas standards. The hydrocarbon concentrations were summed and converted to a molar concentration of the precursor using the ideal gas law. Then, a graph of the peak height of a particular infrared band versus the precursor concentration was prepared. From the slope of the resulting straight line, a calibration factor relating the intensity of the infrared band to the precursor concentration was obtained. Using this calibration factor, the organometallic concentrations were calculated from the measured infrared peak heights.

In the following section, the results are discussed in terms of the relative pressure of an organometallic compound in the gas effluent of the MOVPE reactor. The relative pressure is defined as x_i , where

$$x_i = \frac{P_i}{P_{\text{TMIIn}}^0 + P_{\text{TEGa}}^0}. \quad (1)$$

Here, P_i is the partial pressure of the i th organometallic compound, and the superscript 0 refers to the partial pressures of the sources (TEGa and TMIIn) initially introduced into the gas manifold.

Each InGaAs film was analyzed over the length of the glass reactor tube using a $\theta/2\theta$ scan on a Crystal Logic powder diffractometer. The tube was sectioned into 1 cm pieces, which were split axially to reveal the film on the inner wall. Diffraction patterns were obtained by scanning for the (1 1 1) and (3 1 1) peaks at 2θ ranges of 24°–29° and 48°–55°, respectively, in steps of 0.01°. Using Vegard's law and the measured peak position, the In_{*y*}Ga_{1–*y*}As film composition was calculated from

$$y = \frac{a - a_{\text{GaAs}}}{a_{\text{InAs}} - a_{\text{GaAs}}}, \quad (2)$$

where a is the lattice constant found by Bragg's law, a_{GaAs} is the lattice constant of GaAs (5.6532 Å), and

a_{InAs} is the lattice constant of InAs (6.0584 Å). The peak position was taken to be 2θ corresponding to the maximum intensity value after the diffraction pattern was smoothed to reduce the noise. The value of γ is calculated to within 5% error.

3. Results

3.1. Ligand exchange reactions

Fig. 1 shows the infrared spectra of a mixture of TEGa and TMIn as a function of the relative pressure of TMIn initially fed to the reactor, x_{TMIn}^0 . The absorption bands appearing between 850 and 450 cm^{-1} are characteristic of the individual organometallic molecules in the gas. The bands occurring in this frequency range are due to the C–H bending modes of the alkyl ligands (850–550 cm^{-1}) and the stretching modes of the metal–carbon bonds (750–450 cm^{-1}) [12,13]. A comparison of the infrared spectra of the mixtures, x_{TMIn}^0 equal to 0.3 and 0.7, to those of the pure compounds, x_{TMIn}^0 equal to 0.0 and 1.0, reveals that they are not a simple weighted summation of the infrared spectra of the latter compounds. Instead, they con-

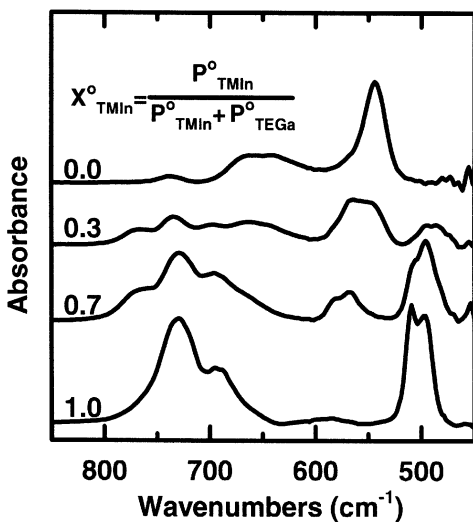


Fig. 1. Infrared spectra of the organometallic compounds in the reactor feed during InGaAs MOVPE at varying ratios of TEGa to TMIn.

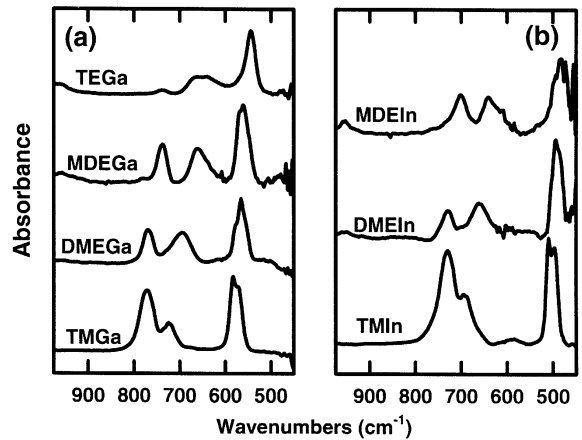


Fig. 2. Infrared spectra of the individual organometallic compounds in the feed after mixing TMIn and TEGa, (a) the organogallium species, and (b) the organoindium species.

tain several new absorption bands near 770 cm^{-1} , between 590 and 550 cm^{-1} , and between 500 and 475 cm^{-1} .

The new bands show similarities with those of the TEGa and TMIn sources initially fed, suggesting the formation of new organometallic compounds by ligand exchange reactions [9]. Five new organometallic compounds are identified from the reaction between TEGa and TMIn. The infrared spectra of each organometallic compound in the mixture are shown in Fig. 2. The band positions in the spectral region between 850 and 450 cm^{-1} and the proposed assignments for all the modes are summarized in Table 1. The infrared spectra of the individual compounds are obtained from the mixture by spectral subtraction, as described elsewhere [9]. One of the infrared spectra is identical to the known vibrational spectrum of TMGa [14]. On the other hand, the characteristic In–C stretch at 470 cm^{-1} for triethylindium (TEIn) is not observed in the mixture, but is included in Table 1 for reference. The measured peak positions for TMIn, TMGa and TEGa agree well with those previously reported in the literature [14–16]. The remaining four species are identified as methyl-diethylgallium (MDEGa), dimethylethylgallium (DMEGa), methyl-diethylindium (MDEIn), and dimethylethylindium (DMEIn), which are the obvious products of ligand exchange between TEGa and TMIn.

Table 1
Infrared band assignments of the organometallic compounds for the spectral region between 900 and 450 cm^{-1}

Mode ^a	Organometallic compounds							
	TMGa	DMEGa	MDEGa	TEGa	TMIn	DMEIn	MDEIn	TEIn ^b
$\nu(\text{MC}) - \text{P}$	583	578	569	544	497	494	486	470
$\nu(\text{MC}) - \text{R}$	570	565	560		509			
$\rho(\text{CH}_3)(e')$	771	769	739	738	729	728	700	–
$\rho(\text{CH}_3)(a_2')$	723	694	661	652	693	660	640	–

^a $\nu(\text{MC})$ refers to the asymmetrical metal–carbon stretching mode, which shows a P- and R-branch in the gas-phase (no Q-branch is observed), $\rho(\text{CH}_3)$ refers to the CH_3 rocking mode with either the e' symmetry or the a_2' symmetry.

^bData obtained from Ref. [12].

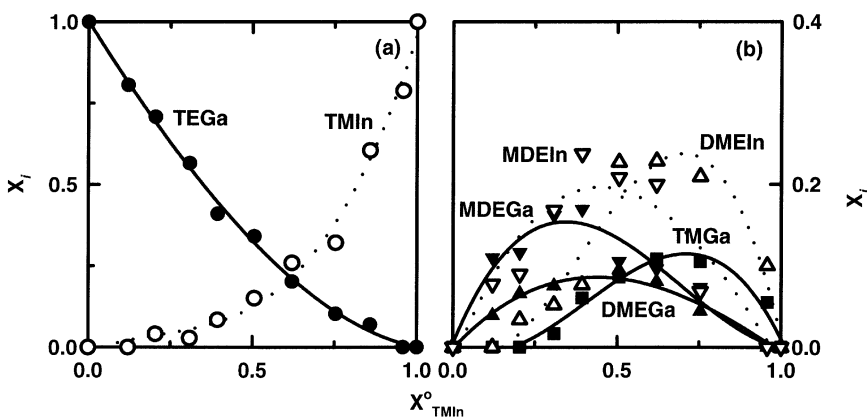


Fig. 3. The dependence of the relative partial pressures of each organometallic compound in the gas on the initial relative pressure of TMIn fed at 80°C. Note the different ordinate scales in (a) and (b).

Ligand exchange reactions have a profound effect on the composition of the reactor feed. Fig. 3a shows the dependence of the relative pressures of TEGa and TMIn in the mixture on the initial relative pressure of TMIn, x_{TMIn}^0 , for reactor and feed lines held at 80°C. The curves are concave up because the concentrations of these two precursors in the mixture are less than the amount initially fed. The decrease in the concentration of TMIn is more severe than that for TEGa, as evidenced by the extent to which each curve deviates from its respective diagonal line. Shown in Fig. 3b are the relative pressures of the exchange products for different mixtures of TEGa with TMIn. Inspection of these data reveals that the relative concentrations of the exchange products vary significantly

with x_{TMIn}^0 . For example, after mixing TMIn and TEGa at $x_{\text{TMIn}}^0 = 0.3$, the main reaction products are MDEIn and MDEGa. Conversely, at $x_{\text{TMIn}}^0 = 0.6$, the organoindium compounds present are TMIn, DMEIn and MDEIn, while the organogallium species are distributed equally among TMGa, DMEGa, MDEGa and TEGa.

The dependence of the relative pressures of the organometallic sources on the reactor temperature is shown in Fig. 4 for $x_{\text{TMIn}}^0 = 0.6$. No changes are observed in the relative pressures between room temperature and 200°C. At 250°C, the organoindium species start to decompose, and by 400°C, they are completely depleted from the gas phase (Fig. 4b). The order in which the indium species decompose ($\text{MDEIn} > \text{DMEIn} > \text{TMIn}$)

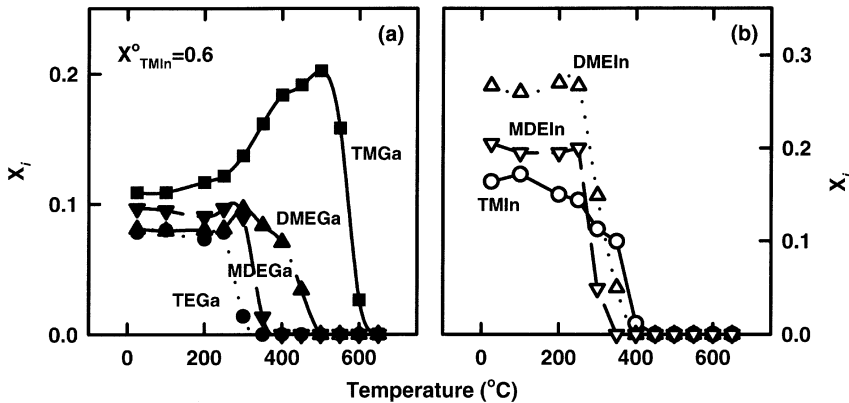


Fig. 4. The dependence of the relative pressures of (a) the organogallium species and (b) the organoindium species in the reactor outlet as a function of temperature for $x_{\text{TMin}}^0 = 0.6$. Note the different ordinate scales in (a) and (b).

corresponds with the thermal reactivity of the molecules, i.e., the species with more methyl ligands are less reactive. The trend observed in Fig. 4a for the decomposition of the different organogallium compounds is the same as that of the indium species, i.e., the order of reactivity is $\text{TEGa} > \text{MDEGa} > \text{DMEGa} > \text{TMGa}$. Triethylgallium and methyl-diethylgallium decompose in the same temperature range as the indium species. However, DMEGa and TMGa do not pyrolyze until 400°C and 500°C, respectively, and between 250°C and 500°C, we observe a doubling of the relative pressure of TMGa. Evidently, the decomposition reactions of the other sources stimulate the production of trimethylgallium.

3.2. InGaAs MOVPE

The formation of new organoindium and organogallium compounds from the initial TEGa and TMin sources influences the InGaAs MOVPE process considerably. Although the residence time during the growth experiments is five times higher than that during the pyrolysis experiments, the general trend is the same. Fig. 5 shows the effect of the growth temperature on the composition of the film at different axial positions in the reactor for InGaAs MOVPE with TEGa, TMin and TBAs at a V/III ratio of 40, a total group III partial pressure of 7×10^{-2} Torr, and an x_{TMin}^0 value of 0.5. The

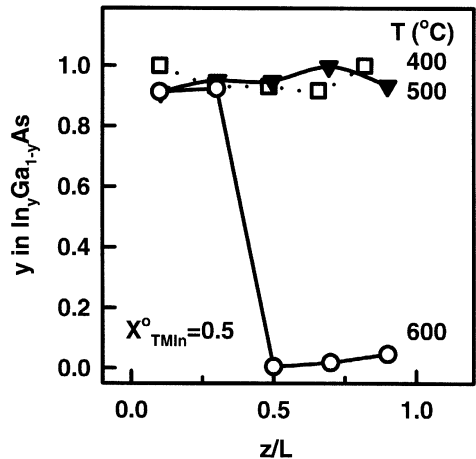


Fig. 5. The dependence of the In mole fraction in the film on the relative axial position in the reactor at growth temperatures of 400°C, 500°C and 600°C, and $x_{\text{TMin}}^0 = 0.5$.

graph indicates that for this feed composition, severe film segregation occurs at 600°C with the film near the inlet consisting of InAs and the film near the outlet consisting of GaAs. It should be noted that under these conditions, all the group III compounds are depleted from the gas by the exit of the reactor. At 400°C and 500°C, the conversion of the organometallic sources is much lower. However, in this case, very little gallium is incorporated into the film over the length of the reactor. Infrared analysis

of the effluent gas reveals that the relative pressure of TMGa has doubled, while the relative pressure of DMEGa has not changed. These results indicate that the small amount of gallium that incorporates into the film at 400°C and 500°C, originates from the decomposition of TEGa and MDEGa.

Gallium is increasingly incorporated into the film when the feed composition is more abundant in reactive ethylgallium species. This is shown in Fig. 6, where the In mole fraction in the film is plotted as a function of the feed composition at different axial positions in the reactor. In this experiment, InGaAs was deposited at 500°C, a total group III partial pressure of 7×10^{-2} Torr, a V/III ratio of 40, and x_{TMIIn}^0 values of 0.2, 0.3, and 0.5. At $x_{\text{TMIIn}}^0 = 0.5$, the film contains more than 90 mol% In at all positions within the reactor. By increasing the fraction of organogallium species in the feed, i.e., lowering x_{TMIIn}^0 to 0.3 or 0.2, the In content of the films decreases to an average value of 60 to 80 mol%. However, the alloy composition is not homogeneously distributed in this case. Instead, the mole fraction of indium in the film declines from 1.0 at the reactor inlet to 0.45 or 0.65 at the reactor outlet. Similar experiments carried out at 400°C resulted in InAs growth only.

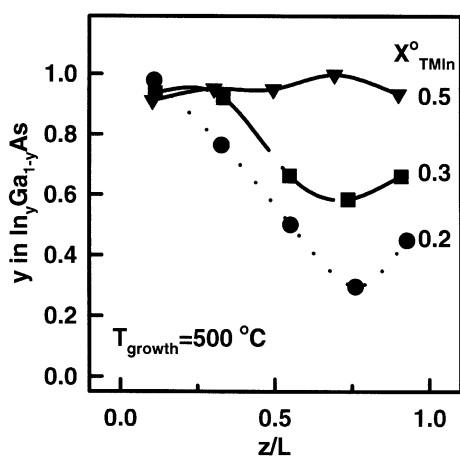


Fig. 6. The dependence of the In mole fraction in the film on the relative axial position in the reactor at different x_{TMIIn}^0 values, and a growth temperature of 500°C.

4. Discussion

4.1. Alkyl ligand exchange

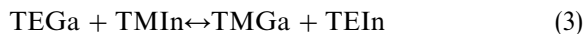
Few efforts have been made to investigate the exchange reactions of organogallium and organoindium compounds. Ligand exchange has been shown to occur between TMGa or TMIIn and trimethylaluminum in hydrocarbon solutions using the technique of line broadening in the proton NMR spectra of the individual species [17]. In the same study, it is mentioned that TMGa and TMIIn rapidly exchange their methyl groups in toluene at -65°C . The necessity to study this reaction at such a low temperature indicates that the ligands exchange very rapidly. Exchange reactions between TMGa with TEGa [18], and in mixtures of Group II dialkyls and TMIIn or TMGa were also studied using NMR techniques [18,19]. Again, these results indicate that alkyl exchange is extremely fast, and that sample solutions had to be cooled to -60°C or -85°C in order to slow down the reaction rates to a speed that could be measured by NMR. In these systems, the apparent activation energy for exchange is less than 10 kcal/mol [18].

Evidence for ligand exchange reactions in the gas phase was found by Jones and co-workers [8,20]. It was observed that TMGa and TMIIn react with trimethylamine alane (TMMA, $\text{AlH}_3 - \text{N}(\text{CH}_3)_3$) in the feed lines of the MOVPE reactor, producing a number of different (TMA-complexed) methylaluminum, alkylgalliumhydride, and alkylindiumhydride species. More recently, we found that DEZn and DMCd rapidly exchange their alkyl ligands in the feed lines of a CdZnTe MOVPE reactor [9,21]. The gas-phase reaction products are methylethylzinc, dimethylzinc, methylethylcadmium and diethylcadmium. Thus, alkyl ligand exchange is a general reaction that occurs in mixtures of electron-deficient group II and III organometallic compounds in both the liquid and gas phases. Our infrared results on ligand exchange reactions between TEGa and TMIIn are consistent with these prior studies.

The assignment of the observed infrared bands to specific exchange products is based on the analysis of the infrared data as well as on the relative

thermal stabilities of the compounds. The peak position of the vibrational modes of MDEGa, DMEGa, MDEIn and DMEIn show trends similar to those of mixed alkyl complexes of zinc [9], cadmium [9], lead [22], germanium [23] and arsenic [24,25]. In these latter studies, the values of the metal–carbon stretching frequencies for the mixed alkyl species lie between those of the fully exchanged homologues, and they progress to lower values as the complexes contain fewer and fewer methyl groups. The average values for the P- and R-branches of the In–C and Ga–C stretching frequencies shift in an analogous fashion: from 503 cm^{-1} for TMIIn, to 494 cm^{-1} for DMEIn, to 486 cm^{-1} for MDEIn, to 470 cm^{-1} for TEIn, and from 577 cm^{-1} for TMGa, to 572 cm^{-1} for DMEGa, to 565 cm^{-1} for MDEGa, to 544 cm^{-1} for TEGa (from Table 1). Furthermore, these band assignments are consistent with the thermal stabilities of the ligand exchange products. The reactivity is greatest for the ethyl compounds and least for the methyl ones: $\text{TEGa} > \text{MDEGa} > \text{DMEGa} > \text{TMGa}$, and $\text{MDEIn} > \text{DMEIn} > \text{TMIIn}$.

The distribution of the reaction products in the final mixture strongly depends on the composition of the initial mixture. The general trend observed in Fig. 3 corresponds with the theoretical equilibrium curves as calculated by Moedritzer [26]. The curves of TEGa and TMIIn are concave up due to the formation of the mixed alkyl species. Relatively more TMIIn is consumed by the reaction than TEGa. Qualitatively, this can be explained by the relative abundance of TMGa and the absence of TEIn from the mixture. The formation of one TMGa molecule creates the equivalent of one DMEIn and one MDEIn molecule, based on a mass balance on the methyl ligands. This lowers the concentration of TMIIn more than that of TEGa. Quantitatively, this indicates that the equilibrium constant for the reaction



is less than unity. The standard Gibbs free energy of this reaction must be larger than about 4 kcal/mol, given that the TEIn is present in undetectable amounts.

4.2. InGaAs MOVPE

Ligand exchange reactions are responsible for the inhomogeneous distribution of group III elements in the InGaAs films grown by MOVPE. As shown in Fig. 5, InGaAs deposited at 400°C and 500°C , with equal amounts of TEGa and TMIIn fed, contains between 90% and 100% indium. Examination of Fig. 4 reveals that all the indium compounds decompose at these temperatures, whereas the gallium compounds are converted into TMGa, which does not react. It is likely that the TMGa is produced by a surface reaction of adsorbed Ga and methyl groups, since several researchers have shown that TMIIn decomposes on GaAs (001) surfaces with the production of adsorbed In, hydrocarbons and TMGa [27,28]. Increasing the growth temperature to 600°C leads to TMGa decomposition and more gallium incorporation. However, because the indium compounds are so much more reactive, InAs is deposited in the first half of the reactor, and GaAs is deposited in the second half.

The amount of gallium incorporated into InGaAs films grown at 500°C can be increased by lowering the relative amount of TMIIn introduced into the feed gas, i.e., decreasing x_{TMIIn}^0 . These results are summarized in Fig. 6. This shifts the exchange equilibrium to favor the retention of more ethyl containing gallium compounds. These ethylgallium compounds decompose at 500°C and allow more Ga to be incorporated into the film. Nevertheless, as can be seen in Fig. 6, the reaction kinetics still favor indium deposition upstream and gallium deposition downstream.

Previously, a number of combinations of gallium and indium precursors have been examined for InGaAs growth. High-quality films have been deposited at 550°C using TEGa and TEIn [29], and at higher temperatures using the combinations TMGa/TMIIn [5–7], and TMGa/DMEIn [30]. Mixed results were obtained in atmospheric pressure systems using TMGa and TEIn as the sources. High-quality InGaAs films with good compositional uniformity were obtained by Andre et al. [31], while in another study, Ludowise et al. [5] observed InGaAs film segregation. With TMIIn and TMGa, the latter workers were able to grow

uniform InGaAs films in both thickness and composition. However, when TEIn with TMGa was used, the growth rate at 600°C decreased from 8.3 to 3.7 Å s⁻¹ from the front to the back of the 3-cm long wafer. In addition, the composition of the In_yGa_{1-y}As decreased from $y = 0.24$ at the front of the wafer to $y = 0.06$ at the back of the wafer. These latter results are comparable to what we observe using TEGa and TMIn. In all the studies in which the group III sources have mixed ligands, exchange reactions take place when the sources are mixed prior to entering the reactor. Depending on the reactor design and the growth conditions, exchange reactions cause the composition and thickness of an alloy film to vary uncontrollably across the surface of a wafer.

High-performance InGaAs/InP and InGaP/GaAs heterojunction bipolar transistors (HBTs) contain thin layers that are heavily doped with acceptors between 10¹⁹ and 10²⁰ cm⁻³. Carbon acceptor doping at these levels is achieved by carrying out the MOVPE process at 425°C to 475°C and using CCl₄ or CBr₄ as the carbon precursor [2–4]. At these low growth temperatures, TMGa is relatively unreactive, and probably should not be the Ga source. Since ligand exchange reactions will produce TMGa from TMIn and any other organogallium compound, TMIn should not be used for low-temperature InGaAs growth either. This suggests that for the MOVPE of HBT structures, one should select combinations of sources that do not contain methyl ligands, such as TEGa and TEIn, or triisobutylgallium (TIBGa) and triisopropylindium (TIPIn). In the case of these latter two sources, ligand exchange between the isobutyl and the isopropyl groups should not generate organometallic compounds with widely different thermal stabilities. We are currently investigating the low-temperature MOVPE of InGaAs/InP using these alternative precursors.

5. Conclusions

Ligand exchange reactions have been observed between TMIn and TEGa in the feed lines to the MOVPE reactor. The products of these reactions are MDEIn, DEMIn, MDEGa, DMEGa, and

TMGa. The new organoindium precursors decompose between 250°C and 400°C, while the new organogallium precursors decompose between 250°C and 600°C. In our MOVPE reactor, this large difference in the reactivity of the sources leads to films that are rich in indium near the reactor inlet and rich in gallium near the reactor outlet.

Acknowledgements

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