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Kinetics of carbon tetrachloride decomposition during the metalorganic vapor-phase epitaxy of gallium arsenide and indium arsenide

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Abstract

Carbon tetrachloride is used to dope gallium arsenide and indium–gallium arsenide films with carbon during metalorganic vapor-phase epitaxy (MOVPE). In this study, the decomposition kinetics of CCl_4 and of the other precursors (triethylgallium, trimethylindium and tertiarybutylarsine) were determined by monitoring the reactor feed and effluent gases with on-line infrared and mass spectroscopies. As the CCl_4 partial pressure was increased from 1×10^{-4} to 3×10^{-3} atm, the GaAs growth rate decreased and eventually fell to zero. Most of the reduction in growth rate (80 to 95%) was due to a surface reaction between adsorbed gallium and chlorine to produce volatile GaCl. The etching of the GaAs film by adsorbed chlorine to produce $GaCl_3$ accounted for the remainder of the growth rate reduction. The latter reaction was insignificant below a threshold CCl_4 partial pressure of $\sim1.5\times10^{-3}$ atm at 450°C and $\sim8.0\times10^{-4}$ atm at 550°C. A comparison of GaAs and InAs MOVPE revealed that the reaction of CCl_4 with indium to form volatile metal chlorides was nearly 10 times faster than the equivalent reactions with gallium. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the manufacture of GaAs/AlGaAs and InGaAs/InP heterojunction bipolar transistors (HBTs) by metalorganic vapor-phase epitaxy (MOVPE), heavy p-type doping of the GaAs or InGaAs base layer is necessary [1–3]. Carbon is the preferred p-type dopant due to its low diffusivity compared to zinc and beryllium [4–7]. Carbon tetrachloride is an efficient MOVPE source for incorporating carbon into GaAs and InGaAs [8–21]. Under certain conditions, essentially all the carbon deposited inserts into the acceptor sites of GaAs. However, CCl_4 also reacts with gallium and indium at the film surface, producing volatile metal chlorides [19,21]. The rates of these reactions are

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highly temperature dependent, so that small variations in the substrate temperature from both run to run and from the center to the edge of the wafer can generate films of nonuniform composition.

Previous studies have shown that the amount of carbon incorporated into GaAs increases with decreasing substrate temperature, decreasing V/III ratio, and increasing CCl_4 partial pressure [10,13,15]. Using isotopically labelled trimethylgallium, Buchan et al. [13] found that carbon tetrachloride is the source of the dopant in the film, and that it most likely incorporates via a heterogeneous reaction on the semiconductor surface. A reduction in growth rate is also observed with increasing CCl_4 partial pressure, and at high enough pressures, film growth ceases altogether [14,19,21]. This has been attributed either to the reaction of chlorine with the gallium source, or to chlorine etching of the gallium arsenide films.

The research conducted to date on carbon doping with CCl_4 has established the relationship between the process conditions and the film growth rate, as well as the carbon doping level in the film. In addition, Li et al. [22] have identified the decomposition mechanism of CCl_4 on GaAs(0 0 1) surfaces under ultrahigh vacuum. However, the effects of this dopant source on the reactions of other organometallic precursors present during MOVPE have not been examined. We have addressed this problem by monitoring the decomposition rates of the sources during GaAs and InAs MOVPE using triethylgallium, trimethylindium, tertiarybutylarsine and carbon tetrachloride. We have discovered that a surface reaction between adsorbed chlorine and gallium (or indium) is responsible for the reduction in the growth rate, and that under most conditions, film etching is a minor reaction pathway. Furthermore, this study demonstrates that the addition of a dopant precursor to the reaction mixture can have a profound effect on the decomposition chemistry of all the organometallic reagents used in the MOVPE process.

2. Experimental methods

The growth experiments were carried out in a low-pressure MOVPE reactor operated at 450–650°C, $1.0–30.0 \times 10^{-4}$ atm of triethylgallium (TEGa), $1.0–30.0 \times 10^{-4}$ atm of trimethylindium (TMIn), $1.0–50.0 \times 10^{-4}$ atm of carbon tetrachloride (CCl_4), V/III ratios from 15 to 50, residence times from 0.005 to 0.4 s, and a total pressure of 0.13 atm. Electronic-grade TEGa, TMIn and TBAs were used as the organometallic sources, and the hydrogen carrier gas was purified through a palladium membrane. Films were deposited on the inner walls of quartz tubes, 0.4 cm in diameter. A cylindrical heating element, 6 cm in length, with a recess allowing a thermocouple to contact the outer quartz wall, was positioned at the center of the 20 cm tube. Water-cooled heat exchangers, 6 cm in length, were positioned adjacent to the heating element, producing a well-defined hot zone.

For laminar flow in cylindrical tubes, the thermal entrance length may be estimated from the well-known correlation, $L_{ent}/D = 0.5$ RePr [23]. The Reynolds number ranged from 0.6 to 50 (corresponding to residence times from 0.4 to 0.005 s), and the Prandtl number was 0.7. These dimensionless groups were evaluated at an entrance temperature of ~ 300 K. Based on these values, the entrance length ranged from a maximum of 12% to a minimum of 0.14% of the total reactor length, justifying our assumption of an isothermal reactor.

The consumption rates of the organometallic sources were determined by monitoring the gas-phase composition of the reactor feed and effluent with a Leybold Transpector 300 amu mass spectrometer and a BioRad FTS-7 infrared spectrometer. The infrared spectra of the gas streams were collected in a small flow cell (17.7 cm long by 3.0 cm in diameter) that was sealed with KBr windows. Intense vibrational bands of TBAs, TEGa, TMIn, and CCl_4 were detected at 2093, 544, 497, and 793 cm^{-1}, respectively. The bands were well resolved and provided a means of independently monitoring the consumption of each reactant during MOVPE [24].

Infrared 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 concentrations through the following calibration procedure. Precursor concentrations were determined by mass spectrometry, measuring the hydrocarbons produced during

complete pyrolysis of each organometallic compound at 600°C. The mass spectrometer signals were calibrated using hydrocarbon standards. Then, the hydrocarbon concentrations were summed and converted to a molar concentration of a given precursor. Finally, a graph of the peak height of a characteristic 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. The consumption rate, r_i, of a source was calculated from the following expression:

$$r_i = Q \times [c_{if} - c_{ie}], \quad (1)$$

where Q is the volumetric flow rate, and c_{if} and c_{ie} are the feed and effluent concentrations of source i.

The gallium arsenide net growth rate was determined by weighing the quartz tube before and after the deposition of a film. Prior to the last weight measurement, the tube was rinsed with a 0.1 M HCl solution to remove any products that condensed downstream of the reaction zone. The indium arsenide net growth rate could not be determined in this manner because InAs is soluble in HCl.

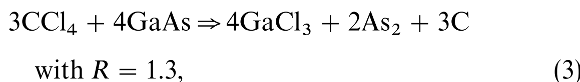
For MOVPE of gallium arsenide with CCl_4, the dependence of the consumption rate of a source on the surface temperature and gas-phase concentrations of the organometallic species can be expressed as follows:

$$r_i = A \exp\left(-\frac{E_a}{RT}\right)\left(\frac{P^x_{TEGa}P^y_{TBAs}P^z_{CCl_4}}{(P_T)^{(x+y+z)}}\right)C_T. \quad (2)$$

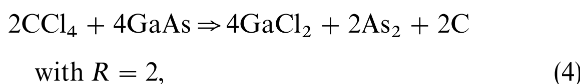
In this equation, A and E_a are the apparent frequency factor (s^{-1}) and activation energy ($kJ\,mol^{-1}$), R is the ideal gas constant ($kJ\,mol^{-1}\,K^{-1}$), T is the temperature (K), C_T is the total molar concentration of the gas ($mol\,L^{-1}$), P_T is the total pressure (atm), P_{TEGa}, P_{TBAs}, and P_{CCl_4} are the partial pressures of the three reactants (atm), and x, y and z are their reaction orders. It is apparent from Eq. (2) that to determine an accurate activation energy, the partial pressure of each organometallic precursor must remain constant within the reactor. Accordingly, the reactor was operated under conditions where the conversion of the limiting reagent was held to less than 10%. This was accomplished by offsetting any increase in reaction rate with an increase in the total flow rate.

3. Results

Plotted in Fig. 1 is the relationship between the GaAs etching rate and the CCl_4 consumption rate. In this experiment, a film of gallium arsenide was deposited in a glass tube, and its weight taken. Then 6.5×10^{-4} atm of carbon tetrachloride in 0.13 atm of hydrogen was passed over the film at temperatures ranging from 400 to 500°C. After a given period of time, the reaction was stopped and the tube weighed again. The amount of GaAs etched by the CCl_4 was calculated from the difference in film mass. It is evident from the figure that the etch rate of GaAs increases linearly with the CCl_4 consumption rate. The slope of the line represents the number of Ga atoms etched per CCl_4 molecule reacted. There are three possible reactions:



$$3CCl_4 + 4GaAs \Rightarrow 4GaCl_3 + 2As_2 + 3C \quad \text{with } R = 1.3, \quad (3)$$



$$2CCl_4 + 4GaAs \Rightarrow 4GaCl_2 + 2As_2 + 2C \quad \text{with } R = 2, \quad (4)$$

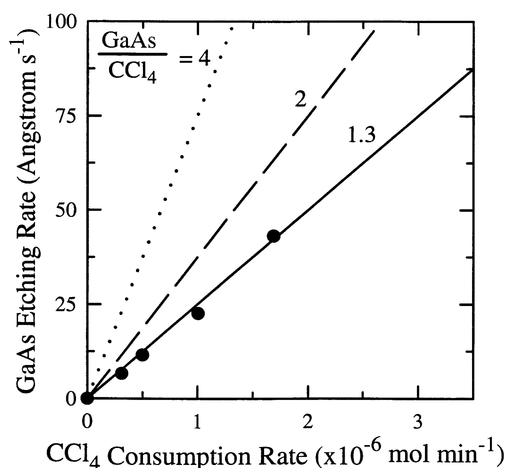


Fig. 1. The dependence of the etch rate of GaAs on the CCl_4 consumption rate at different temperatures in H_2 carrier gas.

$$CCl_4 + 4GaAs \Rightarrow 4GaCl + 2As_2 + C$$

with $R = 4$. (5)

In these mechanisms, R is the molar ratio of GaAs to CCl_4. There is no evidence for the partial decomposition of CCl_4 (which would yield a lower R-value for the same amount of GaAs), because no chlorinated hydrocarbons, other than CCl_4, were detected by MS or IR spectroscopy in the reactor effluent. For InAs etching, the reactions are of the same form, substituting In for Ga into each of the equations above.

In Fig. 1, straight lines are plotted for each value of R. It is seen that the data follow $R = 1.3$, indicating $GaCl_3$ is the primary etch product. The activation energy for GaAs etching with CCl_4 was determined to be 70 ± 5 kJ mol^{-1} between 400 and 500°C. It should be noted that the addition of TBAs to the feed gas completely inhibits GaAs etching below 450°C.

Shown in Fig. 2a is the dependence of the consumption rates of carbon tetrachloride and triethylgallium on the TEGa partial pressure. In this experiment, CCl_4, TEGa and H_2 were fed to a reactor containing a GaAs film heated to 450°C. The CCl_4 partial pressure was kept constant at 6.5×10^{-4} atm, while the TEGa partial pressure was varied. The conversion of both sources increases with the partial pressure of the group III source. The reaction orders for the dependence of the TEGa and CCl_4 consumption rates on TEGa partial pressure (i.e., x in Eq. (2)) are 0.6 and 0.7 ± 0.05, respectively. Under these conditions, there is no measurable etching of the gallium arsenide film. The ratio of TEGa consumed to CCl_4 consumed is approximately four, suggesting that GaCl is formed according to reaction (5) above.

Next, a similar experiment was performed in which the CCl_4 partial pressure was varied while holding the TEGa partial pressure constant at 7.5×10^{-4} atm. The effect of the CCl_4 partial pressure on the consumption rates of carbon tetrachloride and triethylgallium are shown in Fig. 2b. In this case, the TEGa consumption rate does not change, while the CCl_4 consumption rate increases with increasing CCl_4 partial pressure. From the slope of the log–log plot, the CCl_4 reaction rate depends on the CCl_4 partial pressure to the 0.2 ± 0.05 power. Once again, no etching of the film was measured.

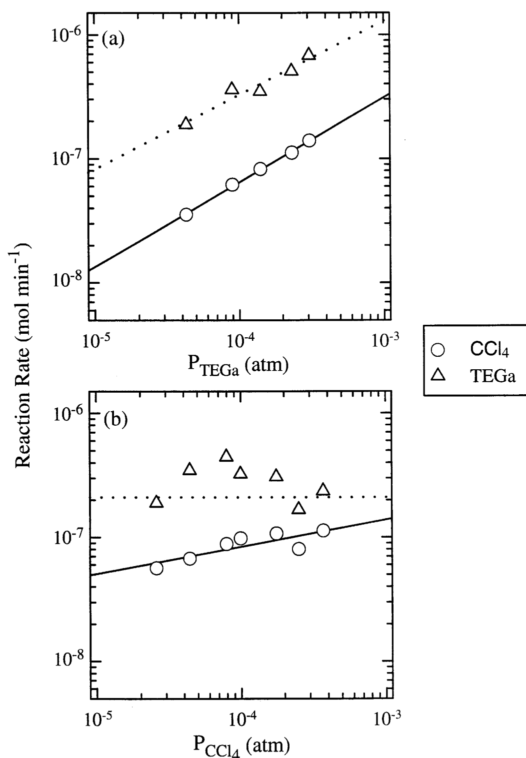


Fig. 2. The dependence of the consumption rates of CCl_4 and TEGa on (a) the TEGa partial pressure and (b) the CCl_4 partial pressure at 450°C in H_2 carrier gas.

In Fig. 3, the dependence of the consumption rates of carbon tetrachloride and trimethylindium on the TMIn partial pressure is presented. Here, an indium arsenide film was grown, and then TMIn, CCl_4 and H_2 were fed to the reactor at 450°C. The CCl_4 partial pressure was held constant at 6.5×10^{-4} atm, while varying the TMIn partial pressure. Inspection of the figure reveals that the reaction rates of both sources increase with the amount of TMIn in the gas. At a TMIn partial pressure near 1×10^{-3} atm, the R-value is approximately four, indicating that InCl is most likely the main reaction product. It should be noted that the reaction of TMIn with CCl_4 is nearly 10 times faster than the reaction of TEGa with CCl_4 at the same experimental conditions.

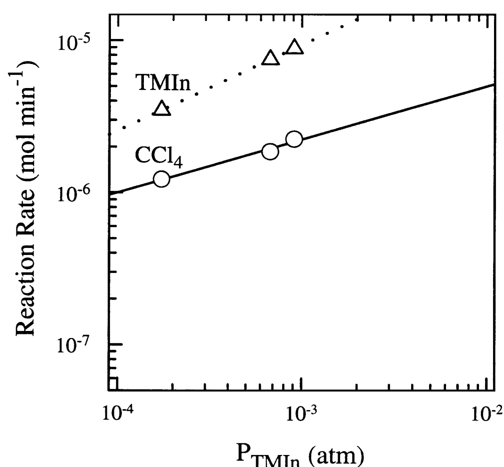


Fig. 3. The dependence of the consumption rates of CCl_4 and TMIn on the TMIn partial pressure at 450°C in H_2 carrier gas.

Presented in Fig. 4 are the dependencies of the TBAs, TEGa and CCl_4 consumption rates, and the GaAs net growth rate on the CCl_4 partial pressure for MOVPE at 450 and 550°C. During this experiment, the TEGa partial pressure was 6.5×10^{-4} atm, the V/III ratio was 15, and the H_2 pressure was 0.13 atm. At both reaction temperatures, the triethylgallium and carbon tetrachloride reaction rates increase, while the tertiarybutylarsine reaction rate decreases with increasing CCl_4 partial pressure. The reaction orders in CCl_4 for the TEGa, CCl_4 and TBAs consumption rates are 0.15, 0.75 and -0.10 ± 0.05, respectively.

The solid curves labelled "$R = 4$" in Fig. 4 represent the case where the growth rate equals the difference between the TEGa consumption rate and four times the CCl_4 consumption rate. In other words, they represent the amount of gallium that remains available for incorporation into the GaAs film if all of the converted CCl_4 reacts with adsorbed Ga to form GaCl. In Fig. 4a, the $R = 4$ curve coincides well with the measured growth rate, suggesting that at 450°C, most of the CCl_4 is consumed to make GaCl in accordance with reaction (5) above. By contrast, at 550°C, the data for net growth rate lie well above the $R = 4$ curve, and this difference increases with increasing CCl_4 partial pressure. Reaction (3), which was observed for

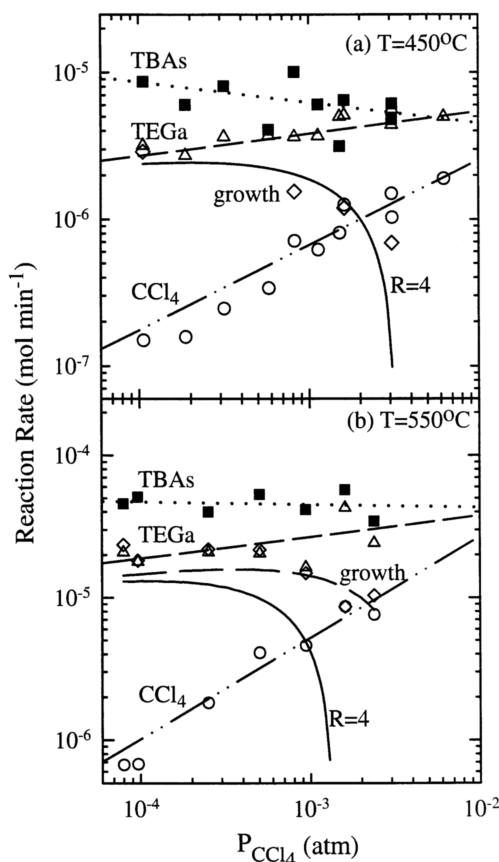


Fig. 4. The dependence of the consumption rates of CCl_4 (○), TEGa (△) and TBAs (■), and of the net growth rate (◇), on the CCl_4 partial pressure during MOVPE of GaAs at (a) 450 and (b) 550°C.

GaAs film etching, consumes less gallium per mole of carbon tetrachloride ($R = 1.3$). It is possible that at 550°C, this reaction increases significantly, so that a greater fraction of the reactive gallium is available for film growth.

The consumption rates of triethylgallium, tertiarybutylarsine, and carbon tetrachloride are nearly an order of magnitude higher at 550°C than those observed at 450°C, but the trends with the CCl_4 partial pressure are the same. At both temperatures, the TBAs consumption rate is greater than the TEGa consumption rate, indicating that film growth is limited by the availability of gallium at the surface. The observed decline in the film growth rate with increasing CCl_4 partial pressure is a result

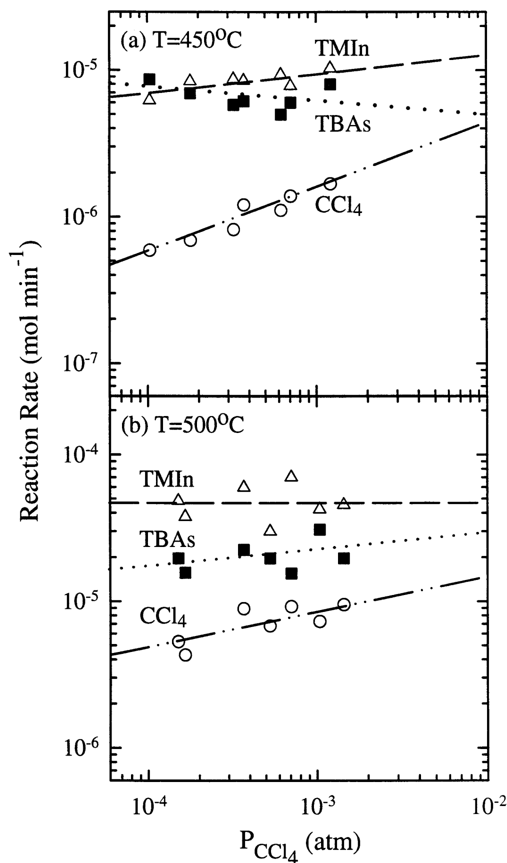


Fig. 5. The dependence of the consumption rates of CCl_4 (○), TMIn (△) and TBAs (■) on the CCl_4 partial pressure during MOVPE of InAs at (a) 450 and (b) 500°C.

of the competing reactions of arsenic and chlorine with gallium. Notice that at the highest CCl_4 partial pressure examined at 450°C, the GaAs growth rate is zero.

Next, MOVPE of indium arsenide in the presence of CCl_4 was examined. Fig. 5 shows the dependence of the consumption rates of trimethylindium, tertiarybutylarsine and carbon tetrachloride on the CCl_4 partial pressure at 450 and 500°C. The growth conditions were identical to those used for MOVPE of gallium arsenide. At 450°C (Fig. 5a), the trends in the consumption rates follow those observed for GaAs growth. However, at $\sim 2\times10^{-4}$ atm of CCl_4, the TMIn consumption rate exceeds that of TBAs, indicating a shift in the limiting reagent for film growth from the group III source to the group V source. The TMIn and TBAs consumption rates depend on the CCl_4 partial pressure to the 0.15 and -0.08 powers, respectively.

At 500°C (Fig. 5b), the trends in the consumption rates are significantly different from those observed at the lower reaction temperature. The consumption rate of trimethylindium exceeds that of tertiarybutylarsine over the entire range of carbon tetrachloride partial pressures. The TMIn and TBAs consumption rates depend on the CCl_4 partial pressure to the 0.03 and 0.10 powers, respectively. Also, the consumption rate of carbon tetrachloride relative to the other two sources is proportionately greater, and does not show a dramatic increase with the CCl_4 partial pressure. These results suggest that a change in the reaction mechanism occurs upon increasing the MOVPE process temperature from 450 to 500°C.

The effect of the V/III ratio on the consumption rates of the organometallic precursors and on the growth rate of GaAs at 450°C is presented in Fig. 6a. To vary the V/III ratio, the tertiarybutylarsine partial pressure was manipulated while the triethylgallium, carbon tetrachloride and hydrogen partial pressures were held constant at 8.0×10^{-4}, 4.0×10^{-4} and 0.13 atm, respectively. As can be seen in the figure, the TBAs reaction rate and the growth rate increase with increasing V/III ratio, while the TEGa and CCl_4 reaction rates decrease. The trend in the growth rate with V/III ratio is in agreement with previous work [21].

In the same way, the effect of the V/III ratio on the consumption rates of TMIn, TBAs, and CCl_4 was investigated. These results are shown in Fig. 6b. The trimethylindium, carbon tetrachloride and hydrogen partial pressures were held constant at 8.0×10^{-4}, 4.0×10^{-4} and 0.13 atm, respectively, while the TBAs partial pressure was varied. In this case, the TBAs and TMIn reaction rates increase, while the CCl_4 consumption rate remains constant with increasing V/III ratio. These results are in contrast to those observed for GaAs MOVPE with CCl_4, where a decline in the group III and IV decomposition rates is observed with increasing V/III ratio (Fig. 6a).

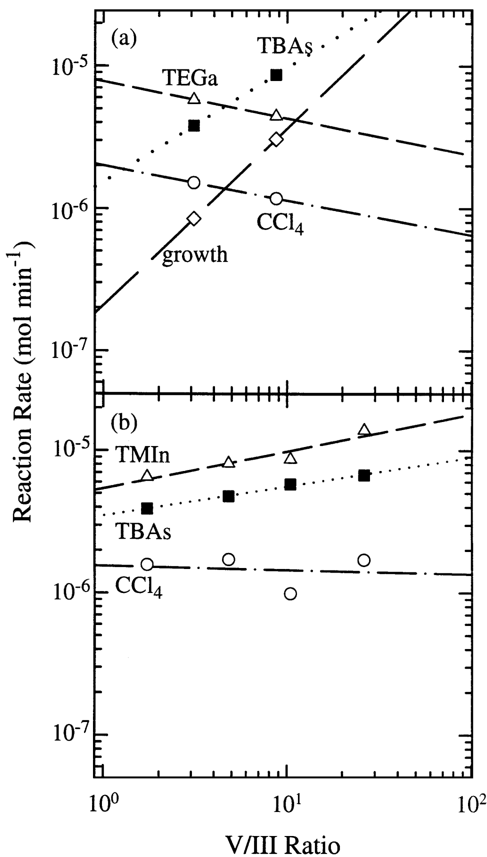


Fig. 6. The dependence of (a) the consumption rates of CCl_4 (○), TEGa (△) and TBAs (■), and of the net growth rate (◇), on the V/III ratio during MOVPE of GaAs at 450°C; and (b) the consumption rates of CCl_4 (○), TMIn (△) and TBAs (■) on the V/III ratio during MOVPE of InAs at 450°C.

4. Discussion

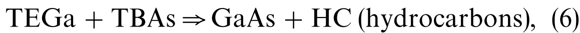
Based on the foregoing results, it is evident that there are three reactions involving gallium and carbon tetrachloride during the MOVPE of gallium arsenide. They are (1) the reaction of adsorbed gallium with arsenic to form GaAs, (2) the reaction of adsorbed gallium with chlorine to form volatile GaCl, and (3) the reaction of adsorbed chlorine with the GaAs film to form volatile $GaCl_3$. In the last case, arsenic will desorb along with the $GaCl_3$ so that film etching occurs. For indium arsenide growth, the same possibilities exist, substituting indium for gallium.

The assertion that $GaCl_3$ is the product of film etching is based primarily on the data plotted in Fig. 1. However, additional evidence for this comes from experiments performed by Bent and coworkers [26], in which steady state Cl_2 etching of gallium arsenide was studied by mass spectrometry in a high vacuum chamber. Their results indicate that for arsenic-rich surfaces, $GaCl_3$ and As_4 are the dominant reaction products. On the other hand, it has been shown that high arsenic coverages greatly reduce the adsorption of CCl_4 on the GaAs(0 0 1) surface [22]. This suggests that As_4 desorption must occur in order to expose underlying gallium atoms to attack by chlorine. Under the experimental conditions of this study, the precursor reaction rates indicate that the GaAs surface is arsenic-rich during MOVPE with CCl_4.

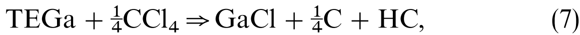
The data plotted in Fig. 2a suggest that gallium monochloride is the product of a surface reaction between chlorine and gallium adsorbed on the surface. The results obtained by Bent and coworkers [26] support this conclusion as well, because they found that GaCl is the primary product during Cl_2 etching of gallium-rich GaAs surfaces. In addition, we have investigated the surface reaction of CCl_4 on the Ga-rich (4×2) reconstruction of GaAs(0 0 1), and have found that GaCl is the main decomposition product [22,27,28].

Gas-phase decomposition of the carbon tetrachloride can safely be ruled out. The frequency factor and activation energy for the reaction $CCl_4 + M \rightarrow CCl_3 + Cl + M$ was determined by Michael et al. [25] to be 1.2×10^{16} $cm^3/mol\,s$ and 43.8 kcal/mol, respectively. To calculate the extent of the gas-phase reaction, it is assumed that "plug flow" occurs in the reactor, and the process is isothermal. A mass balance on the reactor yields the following equation for the conversion of carbon tetrachloride: $([CCl_4]_0 - [CCl_4])/[CCl_4]_0 = 1 - \exp(-k[H_2]L/v)$, where $[CCl_4]_0$ and $[CCl_4]$ are the inlet and outlet CCl_4 concentrations, k is the rate constant, $[H_2]$ is the hydrogen concentration, L is the reactor length, and v is the average velocity. For the longest residence time used, 0.4 s, and the highest reaction temperature, 850 K, the conversion of CCl_4 is < 0.001, confirming that this reaction may be neglected.

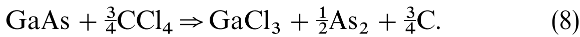
In summary, the three reactions that can occur during GaAs MOVPE with CCl_4 are:



$$\mathrm{TEGa} + \mathrm{TBAs} \Rightarrow \mathrm{GaAs} + \mathrm{HC}\ (\text{hydrocarbons}), \quad (6)$$



$$\mathrm{TEGa} + \tfrac{1}{4}\mathrm{CCl_4} \Rightarrow \mathrm{GaCl} + \tfrac{1}{4}\mathrm{C} + \mathrm{HC}, \quad (7)$$



$$\mathrm{GaAs} + \tfrac{3}{4}\mathrm{CCl_4} \Rightarrow \mathrm{GaCl_3} + \tfrac{1}{2}\mathrm{As_2} + \tfrac{3}{4}\mathrm{C}. \quad (8)$$

These chemical reactions are written such that the coefficients on TEGa and GaAs are one. Note, also, that reaction (7) refers to decomposed TEGa adsorbed on the surface as gallium atoms. Through the application of steady-state mass balances on the reactants and products of these reactions, we obtain the following three relationships:

$$r_{ng} = r_{tg} - r_{etch}, \quad (9)$$

$$r_{TEGa} = r_{tg} + r_{GaCl}, \quad (10)$$

$$r_{CCl_4} = \tfrac{3}{4} r_{etch} + \tfrac{1}{4} r_{GaCl}. \quad (11)$$

On the left-hand side of Eqs. (9)–(11), r_{ng}, r_{TEGa} and r_{CCl_4} are the experimentally determined net growth rate, TEGa consumption rate, and CCl_4 consumption rate. On the right-hand side of the equations are the unknowns, r_{tg}, r_{etch} and r_{GaCl}, which represent the total growth rate, the etch rate, and the GaCl production rate. These three unknowns were determined from the data in Fig. 4 as follows. A best-fit curve through each of the data sets was obtained using power-law functions. Then for a series of CCl_4 partial pressures, values for r_{ng}, r_{TEGa} and r_{CCl_4} were calculated from the functions, and the set of three algebraic equations solved for the unknowns. The solution to these equations were obtained up to a CCl_4 partial pressure where the total growth rate equalled the etch rate. Beyond this point, the solution did not provide a physically meaningful result because the net growth rate was zero.

In Fig. 7, the consumption rates of TEGa and CCl_4 (r_{TEGa} and r_{CCl_4}), the net growth rate (r_{ng}), the total growth rate (r_{tg}), and the production rates of GaCl and $GaCl_3$ (r_{GaCl} and r_{etch}) are plotted as a function of the carbon tetrachloride partial pressure. The latter three rates were obtained from the solution of the coupled mass balances (Eqs. (9)–(11)). Note that the $GaCl_3$ production rate is equivalent to the GaAs etch rate. For GaAs MOVPE at 450°C (Fig. 7a), the curve for r_{tg} superimposes on the curve for r_{ng} up to about 10^{-3} atm of carbon tetrachloride. Above this pressure, there is a slight difference in the two curves. Then at 3×10^{-3} atm of CCl_4, the total growth rate equals the GaAs etch rate, and there is no longer any net growth. Over the range of CCl_4 partial pressures studied, the GaCl formation rate is 20–50 times greater than the $GaCl_3$ formation rate. This indicates that most of the carbon tetrachloride reacts with TEGa (reaction (7)), instead of etching GaAs (reaction (8)). For growth at 550°C (Fig. 7b), the trends are qualitatively the same as at 450°C. However, the curves for the net and total growth rates

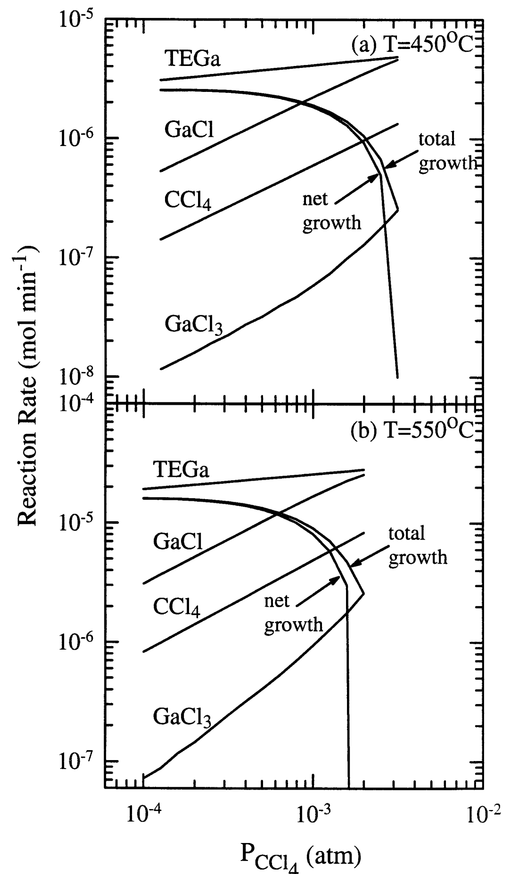


Fig. 7. The effect of the CCl_4 partial pressure on the net and total GaAs growth rates, the TEGa and CCl_4 consumption rates, and the GaCl and $GaCl_3$ production rates at (a) 450 and (b) 550°C, as predicted by the model.

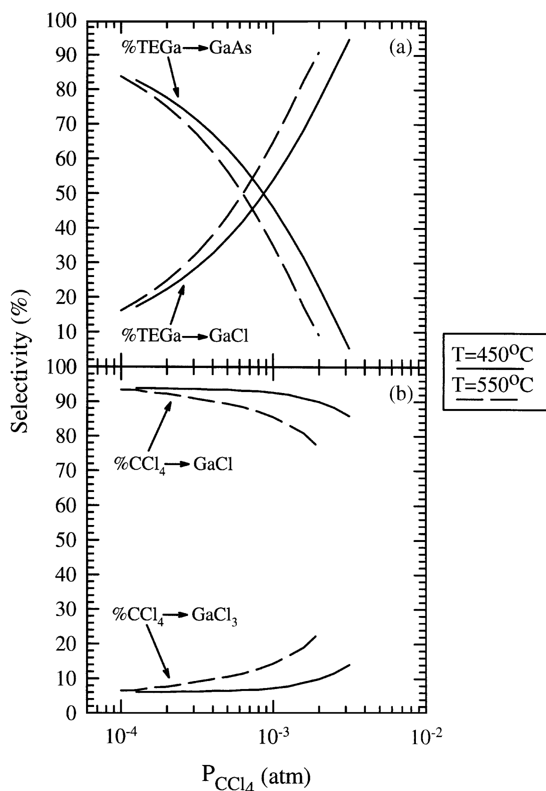


Fig. 8. The effects of the CCl_4 partial pressure and the temperature on (a) the selectivity for TEGa conversion into GaAs or GaCl, and (b) the selectivity of CCl_4 conversion into GaCl or $GaCl_3$.

begin to deviate at a slightly lower CCl_4 partial pressure, $\sim 8\times10^{-4}$ atm, and the cutoff for zero growth rate is shifted down in CCl_4 pressure to about 2×10^{-3} atm.

Fig. 8a displays the percentages of converted triethylgallium contributing to either film growth or gallium monochloride production. These data are plotted against the inlet carbon tetrachloride partial pressure at 450 and 550°C. It is clear that as the CCl_4 partial pressure increases, the amount of adsorbed gallium that is removed from the surface as GaCl increases drastically at the expense of film growth. This tendency is exacerbated at the higher growth temperature. In Fig. 8b, the percentages of converted carbon tetrachloride contributing to either film etching ($GaCl_3$ production), or reaction with adsorbed gallium (GaCl production) are shown as a function of the carbon tetrachloride partial pressure. This plot shows that between 80 and 95% of the converted CCl_4 reacts with the adsorbed gallium, and not with the film. However, upon raising the temperature from 450 to 550°C, a greater percentage of the CCl_4 etches the film, i.e., as much as 20% at 2×10^{-3} atm CCl_4. This trend indicates that the etching reaction is more highly activated than the reaction between adsorbed CCl_4 and TEGa, and becomes more prevalent at high growth temperatures.

In Fig. 9, the ratio r_{etch}/r_{tg} is plotted against the carbon tetrachloride partial pressure at 450 and 550°C. This figure illustrates that there is a threshold pressure for significant film etching by CCl_4. The threshold pressures are estimated to be 2×10^{-3} atm at 450°C and 1×10^{-3} atm at 550°C. It is well known that the MOVPE growth temperature must be reduced during CCl_4 doping of GaAs and InGaAs to limit the amount of film etching that occurs [14,16,19,21]. The results presented in Fig. 9 are in good agreement with these other studies.

A comparison of the data in Fig. 5 to that in Fig. 4 reveals that the trends in the consumption rates of the sources with the CCl_4 partial pressure are similar for InAs and GaAs MOVPE. However, there is one notable difference: the consumption

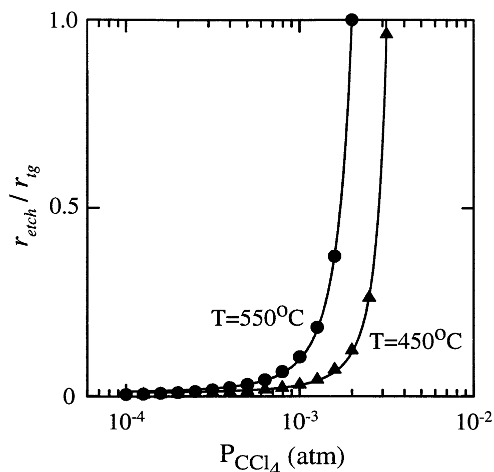


Fig. 9. The ratio of GaAs film etching to the GaAs total growth rate (r_{etch}/r_{tg}) as a function of the CCl_4 partial pressure at 450 and 550°C.

rate of trimethylindium nearly always exceeds that of tertiarybutylarsine, whereas the consumption rate of triethylgallium is below that of TBAs. This means that the InAs films are most likely deposited under indium-rich conditions, instead of arsenic-rich conditions, as is the case for GaAs. Surface science studies of Cl_2 and CCl_4 decomposition on GaAs (0 0 1) have clearly shown that chlorine etching of this material is much faster for a surface that is Ga-rich as opposed to one that is As-rich [26,28]. Therefore, we expect that indium arsenide film etching with carbon tetrachloride is much more severe than with gallium arsenide. Hence, the much greater degree of difficulty encountered in growing carbon-doped InGaAs alloys with CCl_4 [8–10,19].

The reactor configuration used in this study prevented the experimental determination of the carbon levels in the films. Assuming all the carbon tetrachloride that reacts is converted into carbon, the relative rates of CCl_4 consumption and GaAs deposition measured during MOVPE yield molar ratios of carbon to gallium arsenide ranging from 0.05 to 1.00. It is possible that some of the carbon could have been converted into methane or other hydrocarbons. These products could not be distinguished from those generated from the other organometallic sources. It should be noted that no chlorinated hydrocarbons were detected in the reactor effluent steam either by infrared or mass spectroscopy. The C/GaAs ratios calculated from the rate data are obviously too high for acceptor doping of gallium arsenide, and it is likely that most of the carbon produced from the CCl_4 precipitated out as a separate phase. However, reaction rates are consistent with the high partial pressures of the sources employed.

The carbon tetrachloride decomposition kinetics reported herein is consistent with prior studies of MOVPE growth and doping of GaAs with CCl_4. It has been found that the amount of carbon incorporated into the film increases with decreasing substrate temperature, decreasing V/III ratio, and increasing CCl_4 partial pressure [10,13,15]. Similarly, we observe that the ratio of the CCl_4 consumption rate to the net GaAs growth rate increases with decreasing V/III ratio and increasing CCl_4 partial pressure. On the other hand, we do not observe a significant change in r_{CCl_4}/r_{ng} with temperature. Other studies have demonstrated that the carbon levels in gallium arsenide films increase monotonically with the carbon tetrachloride concentration, with apparent reaction orders of 0.75 to 0.8 [14–16]. Our data yield a reaction order for the CCl_4 consumption rate of 0.75 (cf., Fig. 4), which is in excellent agreement with these earlier results. Previous studies have also observed a decrease in the GaAs growth rate with increasing carbon tetrachloride flow rate [14,16,20,21]. Lee et al. [21] found that the growth rate reduction was not due to etching of the GaAs film, but to a reaction of carbon tetrachloride with trimethylgallium. Moreover, they arrived at the same conclusion as we have that GaCl is the most likely product of this reaction.

For epitaxial growth of gallium arsenide on GaAs(0 0 1) substrates, it has been reported that carbon tetrachloride can have either a beneficial or detrimental effect on the film quality, depending on the process conditions. For instance, Kibbler et al. [19] noticed that the surface morphology of carbon-doped GaAs films grown with carbon tetrachloride was shiny below a certain CCl_4 molar flow rate, but became rough at higher concentrations. Other researchers have reported that the introduction of carbon tetrachloride had the effect of improving film quality [14–18,20]. The trends predicted by our model may provide an explanation of this behavior. Specifically, the addition of CCl_4 to the reaction mixture will decrease the growth rate, which in turn should improve the film morphology. On the other hand, we have shown that above a threshold CCl_4 partial pressure, etching via reaction (8) is significant. Several studies have shown that chloride etching of gallium arsenide is anisotropic, and produces pits, which obviously will degrade the film morphology [22,29]. Further experiments are underway to examine the validity of this hypothesis.

5. Conclusions

We have used infrared spectroscopy to monitor the consumption rates of the precursors during the MOVPE of gallium arsenide and indium arsenide. It was found that carbon tetrachloride may either

etch GaAs to produce gallium trichloride, or react with triethylgallium to produce gallium monochloride. The selectivity to each of these reactions during MOVPE was determined using a mass-balance model. This model showed that introducing carbon tetrachloride to the system reduced the growth rate by reacting with the adsorbed TEGa. Gallium arsenide etching was insignificant below a threshold CCl_4 partial pressure of about 10^{-3} atm, and this threshold pressure decreased with increasing temperature. Similar trends in the consumption rates of the sources with CCl_4 partial pressure were observed during InAs and GaAs MOVPE. However, in the former case, the reaction between the group III element and carbon tetrachloride proceeded at a much faster rate.

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