Design of the OMVPE Process

7.1 Consolidated OMVPE Growth Model

In Chapters 2 through 6 we have considered in detail the conceptual underpinnings of our understanding of OMVPE growth in the areas of thermodynamics, physical processes occurring at the surface, reaction kinetics, and mass-transport processes that, together, form the fundamental foundation. Complicating our ability to construct a simple model of OMVPE that is also useful is the fact that so many factors are operative simultaneously during growth. Ultimately, we may be able to construct computer models for the entire process with multiple heterogeneous and homogeneous reactions, with the latter occurring while the molecules are simultaneously being heated and moving through the reactor by convective and diffusive processes. Naturally, the rates of the heterogeneous reactions will have to include the effects of growth parameters on the surface reconstruction and the surface defects such as steps, kinks, islands, and vacancy clusters. Such calculations are clearly not feasible today. The computer power is lacking, even using the largest and fastest machines available. In addition, our collection of kinetic data, while growing, is still nowhere near complete. Early in the twenty-first century, such complete models should make it possible to do computer “experiments” to optimize the process, including selection of the reactor design, reactants, flow rates of the various gases, total pressure, and so forth. For the purposes of this book, it is worthwhile to attempt to construct simple models that describe the experimental observations based on considerations of thermodynamics, mass
transport, and reaction kinetics, with emphasis on the rate-limiting step. This may seem confusing since it is possible that for a given system the growth rate would be limited by mass transport, the macroscopic solid composition by reaction kinetics, and the stoichiometry and dopant incorporation by thermodynamics. However, as we shall see, each process can be treated individually but with essentially complete self-consistency. The goal is to provide an operational paradigm that will allow interpretation of data and rational decisions about optimization of the process.

The complexity inherent in such an undertaking is indicated by the OMVPE growth of GaAsP using TMGa, PH$_3$, and AsH$_3$ as the reactants at a temperature of 650°C and a V/III ratio in the input gas stream of 30. The growth rate, typically \( \leq 0.1 \mu \text{m/min} \), will be controlled by the mass transport of the Ga species to the growth interface. The solid composition is largely controlled by the pyrolysis rates of AsH$_3$ and PH$_3$ via reactions that may involve chemical interactions with the TMGa and/or its pyrolysis products. At the same time, a condition approximating thermodynamic equilibrium is established between the solid and certain vapor species immediately adjacent to the interface. Thus, thermodynamics determines the solid stoichiometry and in many cases dopant incorporation.

In this chapter we will consider in much more detail the system for which the most information is available, the growth of GaAs using various combinations of source molecules. Nearly all of the studies of the GaAs growth process use the "black-box" approach of simply examining the growth rate versus temperature (Figure 7.1), substrate orientation, and the molar flow rates of the nutrient gases to derive information concerning the process controlling the growth rate. We have already discussed in Section 2.3 how the broad outlines of the growth process can be discovered in this way. The growth rate in the low-temperature region has been

![Figure 7.1](attachment:figure7.1.png) Growth efficiency versus temperature for GaAs layers grown by OMVPE using TMGa and AsH$_3$. The data are from Plass et al. [16] (○) at a reactor pressure of 76 Torr; Krautle et al. [13] (●) at atmospheric pressure; and Reep and Ghandhi [9] (■), also at atmospheric pressure. For comparison, the growth rate data for GaAs grown by CBE using TMGa and As are shown (▲). The scale is the growth rate (ML/s) \( \times 1,000 \), with data from Lacklison et al. [52]. (After Stringfellow [59].)
determined to be controlled by reaction kinetics or, perhaps, radical desorption, depending on the conditions, and at higher temperatures by mass transport. We were not able to deduce conclusively the growth-rate-limiting process in the highest temperature range where growth rate decreases with increasing temperature. However, the evidence indicates that either wall deposition upstream from the substrate or homogeneous nucleation competes with the epitaxial growth process to decrease the growth rate. Desorption of Ga species from the surface, a thermodynamic phenomenon, certainly occurs when the temperature is sufficiently high. This is observed routinely for In, which desorbs at lower temperatures.

This broad view does not give information about the reactions occurring during OMVPE. Detailed chemical and kinetic insight into the actual growth reactions can only be obtained from more detailed and sophisticated pyrolysis and growth studies of the type described in Chapter 5. However, even these studies have, to date, not conclusively established the reaction mechanisms.

In this chapter we will attempt to combine the available information of both types to reach the deepest level of understanding of the actual reaction mechanisms. It is worth reminding the reader that a large number of papers deal with basic growth mechanisms. Much of the data are incomplete, and data from various sources are sometimes contradictory. Obviously, an attempt to compare experimental data from dissimilar systems is fraught with difficulty. Nevertheless, development of a detailed understanding of the OMVPE growth process is extremely important. The current incomplete set of data dictates that the most useful approach will be to consider the problem in the broadest context—that is, by considering data obtained using a wide variety of conditions and techniques.

It would be counterproductive to discuss all of the data here; thus, no effort is made to be exhaustive in our treatment of the fundamental aspects of the OMVPE process. We will attempt to extract the salient features of the experimental data and to synthesize this information into a coherent, general picture of the OMVPE growth process. We will see that simple models of the reaction mechanisms explain much of the data. However, as a final caveat, no amount of analysis will allow us to “prove” the simple models of the OMVPE growth process adopted in this chapter, or indeed any model. We can only discuss areas where the models explain the experimental data and point out inconsistencies, indicating the need to improve the models or the experiments. Again, the purpose of developing simple models is to provide a mechanism for interpreting and analyzing experimental data on a daily basis and to provide approaches for the solution of particular problems. In addition, a model encourages the formulation of new questions and thus, ultimately, leads to improved understanding and improved models.

7.1.1 Postulated Reaction Mechanisms

Rather than developing the model for the OMVPE growth of GaAs based on the gradual unfolding of experimental evidence, we will present the model, which
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takes different forms depending on the growth conditions but is based on the same basic mechanism, at the beginning of the discussion. This results in a much clearer treatment of the extremely varied and complex set of data. The general model for growth that seems to conform best to the data also happens to be the oldest bona fide model of the reactions occurring during OMVPE growth. It stems from the work of Schlyer and Ring, who studied very low-temperature surface reactions by observing the methane produced from reactions between adsorbed TMGa and AsH₃ [1]. They postulated the independent adsorption of undecomposed TMGa and AsH₃ with subsequent interactions between adsorbed TMGa and AsH₃ leading to the sequential release of three methane molecules as the temperature was increased. This is believed to be the main growth mechanism at low temperatures and high pressures, as indicated in Table 7.1.

Reep and Ghandhi [2] later added evidence supporting this Langmuir-Hinshelwood (L-H) model, from growth rate studies at higher temperatures more typical of those used for OMVPE growth. However, they postulated homogeneous pyrolysis to occur, resulting in monomethylgallium (CH₃Ga) and AsH reaching the surface. Obviously, the degree to which TMGa pyrolyzes homogeneously to produce monomethylgallium (MMGa) will depend on the temperature and pressure of the reactor. As indicated in Chapter 5, the rapid decomposition of dimethylgallium makes the consideration of this product unnecessary. This model generally agrees with the calculations of Tirtowidjojo and Pollard [3], who determined that at substrate temperatures of 500°C, the growth reactions are essentially completely heterogeneous. By 727°C, homogeneous reactions producing mainly MMGa and some AsH₂ were predicted to occur.

<table>
<thead>
<tr>
<th>Reactor Pressure</th>
<th>Atmospheric</th>
<th>Low (10−760 Torr)</th>
<th>UHV (CBE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Temperature (≤550°C)</td>
<td>L-H, TMGa + AsH₃</td>
<td>L-H, TMGa + AsH₃</td>
<td>Cracked AsH₃ − (2 × 4) TMGa adsorption + pyrolysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₃ desorption</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Uncracked AsH₃ − (4 × 2) No TMGa adsorption + pyrolysis; no growth</td>
</tr>
<tr>
<td>Midtemperatures (550−750°C)</td>
<td>L-H, MMGa + AsH₃; growth limited by mass transport</td>
<td>L-H, TMGa + AsH₃; growth limited by mass transport</td>
<td>Growth rate mainly limited by Ga flux (mass transport)</td>
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<tr>
<td>High temperatures</td>
<td>L-H, MMGa + AsH₃ + products, Ga desorption</td>
<td>L-H, MMGa + AsH₃ + products, Ga desorption</td>
<td>Growth rate limited by Ga flux, Ga desorption</td>
</tr>
</tbody>
</table>

Table 7.1 Mechanism (rate-limiting step) versus growth conditions for GaAs from TMGa and AsH₃
Aspnes et al. [4] performed reflection difference spectroscopy measurements on GaAs surfaces exposed to TMGa, as discussed in Section 5.4.1. Their interpretation of the data indicates that independent TMGa adsorption, desorption, and heterogeneous pyrolysis reactions control the growth rate under certain conditions. These results strongly support the L-H mechanism for OMVPE growth of GaAs using TMGa and AsH₃.

From this and other data to be discussed in this chapter, we conclude that the reaction mechanism must involve predominantly independent (L-H) adsorption of TMGa (or MMGa) and (mainly) AsH₃ followed by surface reactions, in the normal temperature range from 550° to 750° C for reactors operating at atmospheric pressure. As the reactor pressure is reduced, homogeneous reactions become less important; thus, the L-H model involving TMGa + AsH₃ adsorption will extend to even higher temperatures. For OMMBE, the reactions will be completely heterogeneous at all temperatures for all precursors. As discussed later, no growth occurs under these conditions unless the AsH₃ is cracked before reaching the semiconductor surface. Apparently an As-rich \((2 \times 4)\) surface is required for TMGa adsorption and pyrolysis. TMGa is not effectively adsorbed on the Ga-rich \((4 \times 2)\) surface.

At sufficiently high substrate temperatures, the model for AP-OMVPE growth will include homogeneous decomposition of the precursors as the molecules pass through the boundary layer. As mentioned, this yields mainly MMGa when the Ga precursor is TMGa. For less stable precursors such as TEGa, TMIn, and TBAs, homogeneous reactions will have to be considered even for low temperature growth at atmospheric pressure. At the highest temperatures the AsH₃ will decompose to produce the subhydrides AsH and AsH₂, as discussed in Chapter 5.

Reactions between the reactants TMGa and AsH₃ at atmospheric pressure have been postulated to play a role in the pyrolysis reactions [5], as discussed in Sections 5.3.3 and 5.4.5. Support for these interactions was based on indirect evidence, such as the products formed, the ratio of As to Ga pyrolyzed, and the combined pyrolysis temperature being lower than the temperatures for pyrolysis of the individual precursors. As we will see, the evidence appears to demonstrate that such interactions are purely heterogeneous. The observed effects can be explained using the L-H mechanism with no homogeneous TMGa-AsH₃ interactions. Studies of the effects of the precursor partial pressures on growth rate [6, 7] have been interpreted in terms of homogeneous gas phase reactions between the constituents. These effects can be rationalized for heterogeneous reactions simply in terms of the change in surface coverage.

As indicated in Table 7.1, the basic growth reactions are similar for all the growth conditions to be discussed. Differences include the role to which homogeneous processes change the reacting species on the surface and the dependence of the surface structure on growth parameters.
7.2 Kinetically Limited Growth

The discussion of experimental results will be subdivided into the various combinations of temperature and reactor pressure. The mechanism will almost certainly be dependent on the precursors, the temperature, and the system pressure. As already discussed, the use of low temperatures, low pressures, and stable molecules, such as TMGa and AsH₃, leads to heterogeneous mechanisms. For high temperatures, high reactor pressures, and more labile precursors, the pyrolysis reactions will be largely homogeneous.

The low-temperature, kinetically controlled region will be discussed first, moving from atmospheric pressure (760 Torr or 10⁵ Pa) toward the ultrahigh-vacuum OMMBE or CBE regime. A detailed discussion of the low-temperature region may seem academic, since most growth is performed in the midtemperature, mass-transport-limited region. However, success in efforts to lower the growth temperature will depend on an understanding of the OMVPE process that will facilitate the development of source molecules and growth techniques to overcome the kinetic limitations. This regime is also important for atomic-layer epitaxy (ALE), which is virtually always performed at relatively low temperatures. Low-temperature growth is also important for selective epitaxy using labile precursors, where success depends on incomplete pyrolysis at masked surfaces and complete pyrolysis on semiconductor surfaces under exactly the same conditions. In addition, the growth of small-band-gap materials can only proceed at temperatures less than their melting points, which often puts the growth process in the kinetically limited regime, as will be discussed in Chapter 8. Thus, the effort to understand growth in the low-temperature region has practical as well as fundamental implications.

Furthermore, as the total pressure is reduced, mass transport becomes more rapid and surface kinetics become dominant even in the midtemperature regime. This occurs because the mean time between gas-phase collisions increases with decreasing pressure, causing the diffusion coefficient to be inversely proportional to pressure, Equation (6.5), eventually leading to the UHV processes where the source atoms and molecules move from entrance to substrate without collisions. In this case, the growth processes are completely heterogeneous.

Finally, the reaction mechanisms can be studied most directly in the low-temperature regime, where they actually limit the pyrolysis and growth rates. Our understanding of the reactions occurring during growth using typical conditions is based mainly on data obtained at very low reactor pressures over the entire temperature range and at low temperatures in the range of normal OMVPE operation from 10 to 760 Torr. It is reasonable to assume that the reaction mechanisms will be predictable from such kinetic information. This allows a better understanding of the growth processes at normal pressures in the midtemperature regime.
where the reaction kinetics become imperceptible; that is, the black-box approach yields no information about reaction kinetics.

7.2.1 Low Temperature, Atmospheric Pressure

From Arrhenius plots of growth rate versus reciprocal temperature, various authors [2, 8, 9] have deduced the activation energy for the rate limiting step in the low-temperature growth of GaAs from TMGa and AsH_{3} in an atmospheric-pressure reactor to be in the range from 13 to 22 kcal/mol. (We shall consistently use the units of kilocalories per mole. The literature values are sometimes expressed as electron volts [1 eV = 23 kcal/mol] or kilojoules per mole [1 cal = 4.1861 Joule].) Reep and Ghandhi [2] determined a value of 19 kcal/mol for (100) oriented substrates but found the activation energy to vary from 16 kcal/mol for the (111)As orientation to 22 kcal/mol for the (111)Ga orientation. They also determined the activation energy to decrease with increasing input V/III ratio, with values of 20 and 16 kcal/mol at values of V/III ratio of 9.3 and 36.9, respectively [9].

At least part of these variations in activation energy from one set of growth parameters to another and for different substrate orientations is due to the largely heterogeneous nature of the overall OMVPE growth process. As discussed in Sections 3.4.1 and 5.1.3, the measured activation energy for a heterogeneous reaction is the difference between the activation energy for the surface reaction and the enthalpy of adsorption of the reactants. Both will be functions of the bonds formed on the surface (i.e., the orientation of the substrate). The activation energy may also be a function of surface coverage, since interaction between adsorbed species occurs [1] and special sites on the surface may be saturated, as will be discussed later. Thus, a variation of a few kilocalories per mole in activation energy as a function of substrate orientation, V/III ratio, growth rate, and so on, and from one system to another, is not surprising.

The values of activation energy do not, in themselves, specify the OMVPE growth reactions. However, they provide clues about the mechanism and provide a link to the more detailed kinetic studies to be reviewed later in this section, since certain pyrolysis reactions have the same activation energies as the overall growth process.

The study of Reep and Ghandhi [2] provides other useful kinetic data. They studied the growth rate as a function of the reactant partial pressures in the low-temperature, kinetically limited regime. The dependencies for both TMGa and AsH_{3} partial pressures are distinctly sublinear. This was interpreted by Reep and Ghandhi as evidence for high surface coverages in the L-H adsorption model. The rate equation—Equation (3.8)—is given in Section 3.4.1. Naturally, at very high concentrations of the reactants (high growth rates) and low temperatures, desorption of products can limit the growth process. This is clearly seen in Figure 7.2,
where the growth rate determined using in situ GIXS, described in Chapter 3, is used to monitor the growth rate using TMGa and TBAs at temperatures of 520° and 560°C [10]. It is very likely that saturation and desorption limitations apply to special sites on the surface and not the entire surface.

In light of our discussion in Section 3.4.1, care must be exercised in the literal acceptance of the L-H model on several grounds. First, the Langmuir isotherm has long been known to be an excellent tool for inclusion in textbooks, because of its simplicity. However, the model fails to give a good description of adsorption on real surfaces for both metals and nonmetals [11], especially the sublinearity frequently observed. As will be discussed later, the data of Schlyer and Ring [1] indicate the surface coverages are low, especially for AsH₃. Even at room temperature and an AsH₃ pressure of 124.4 Torr, the maximum surface coverage was experimentally determined to be only 0.16. At a temperature of 500°C and an AsH₃ partial pressure of 10⁻³ atm, the conditions that Reep and Ghandhi found to exhibit a saturation of the growth rate with increasing arsine pressure, the AsH₃ surface coverage must be so low that the dependence of surface coverage on partial pressure would be well within the linear range, if all the surface sites were equivalent. The data may be better explained using the physical interpretation of the Freundlich isotherm also discussed in Chapter 5. For a single-crystalline substrate, there are very likely different sorts of surface sites for TMGa and AsH₃ adsorption. It seems quite likely that it is really the steps and/or the kink sites on steps that are active in the crystal growth process. Thus, the saturation observed probably relates solely to the saturation of these key sites on the surface. Most of the surface remains unoccupied. Nevertheless, to conform with common
Arens et al. [12] determined that a change of the ambient from H₂ to He had no appreciable effect on the rate limiting process over the entire range of reactor pressures, including 1 atm, and over the entire temperature range including both mass-transport and kinetic regimes. The ambient apparently plays little or no role in the growth reactions.

Data describing the effect of a change in the As source on the growth process are conflicting. Krautle et al. [13] reported that precracking the AsH₃ by passing it through the heated susceptor gave an activation energy of 35 kcal/mol for the growth process. These results are similar to those of Bhat et al. [14]. Using TMGa and DEAs, which cracks at temperatures much lower than AsH₃, they reported an activation energy of 36 kcal/mol for the temperature range from 412° to 500°C. At even lower temperatures, the activation energy was found to increase to 76 kcal/mol. In contrast, using an elemental As source, Bhat [15] reported an activation energy of 17 kcal/mol, the same as obtained using AsH₃. However, this value is considered less reliable since it is based on only two data points near the mass transport/surface kinetics transition temperature. These data provide direct evidence of heterogeneous interactions between TMGa and AsH₃, or perhaps partially decomposed AsH₃, but not As₂, as part of the rate-limiting step in the OMVPE growth process.

More recently, Plass et al. [16] determined the growth efficiency to be highly dependent on the Ga source molecule in the kinetically limited regime for OMVPE growth of GaAs using either TMGa, TEGa, or TIBGa combined with AsH₃. This is illustrated by the data plotted in Figure 7.3. The data can be interpreted in terms of ascending pyrolysis rates in the order TMGa < TEGa < TIBGa. For example, adsorbed TIBGa is more likely to pyrolyze prior to desorption than is TMGa, hence the higher growth rate for TIBGa. The order of stability is roughly in line with the discussion in Chapter 4. The values of $n^0$ are 0, 1, and 1 for TMGa, TEGa, and TIBGa, respectively. The growth rate for TIBGa is higher, probably because crowding by the large radicals reduces the Ga-isobutyl bond strength, as discussed in Section 4.1. As discussed in detail later, the growth rate under UHV conditions is frequently limited by the desorption of site-blocking species from the surface. However, at atmospheric pressure with high V/III ratios, the removal of the organometallic radicals as alkanes is believed to be more rapid due to the ready availability of atomic H, as discussed in Section 5.4.

Plass et al. [16] suggested that the activation energy is approximately 23 kcal/mol for the three precursors. However, this would be somewhat surprising, since a weaker Ga-C bond should be reflected in a lower value of $E^*$. More likely would be a nearly constant value of the preexponential factor, $A$. This prompts a re-evaluation of the data in Figure 7.3. The growth rate in the low-temperature, kinetically controlled region decreases with increasing stability of the Ga precursor.
The data are not sufficient for an accurate determination of $A$ and $E^*$ for each precursor. However, the lines drawn through the data were calculated on the basis of a constant $A$ factor. They agree with the data at least as well as parallel lines representing a constant value of $E^*$. The resultant values of $E^*$ increase from 22.8 kcal/mol for TIBGa to 27.2 kcal/mol for TMGa. The values of activation energy are nearly equal for TEGa and TIBGa, as might be expected since $n^*$ is unity for both ethyl and isobutyl radicals. However, as discussed, radical crowding decreases the stability of TIBGa relative to TEGa, resulting in the slightly higher low-temperature growth rate for TIBGa.

The growth rate data can be compared with the results of often more detailed pyrolysis studies. In the early studies of Schlyer and Ring [1] the pyrolysis of neat (without diluting gas) mixtures of TMGa plus AsH$_3$ were conducted in a static system. They gave an activation energy of 13 kcal/mol for the heterogeneous pyrolysis of TMGa in the presence of AsH$_3$. At 203°C a single CH$_4$ molecule was produced per molecule of TMGa pyrolyzed. The second CH$_4$ was produced by 259°C, and heating to 420°C was required to produce the third CH$_4$. Methane and
H₂ were the only reaction products. The reaction order was found to be 0.45–0.64 for TMGa and 0.85–0.92 for AsH₃. The authors tentatively concluded that this indicates the reaction to proceed by the Langmuir-Hinshelwood process (i.e., with independent adsorption of the two components before reaction). However, they specifically determined the surface coverage to be small, as mentioned earlier. The coverage must have been considerably smaller during pyrolysis, which weakens the literal conclusion that L-H adsorption is the explanation of the lower-than-unity reaction order. Schlyer and Ring determined the enthalpy of adsorption to decrease with a small increase in surface coverage, which indicates the adsorption processes will not obey the L-H isotherm. The Freundlich isotherm provides a better description of the adsorption processes.

Schlyer and Ring postulated the reaction to occur by formation of an adduct on the surface. The adduct decomposes by sequential elimination of CH₄ molecules that are rapidly desorbed.

The results of the basic pyrolysis studies presented in Chapter 5 are also relevant to the discussion of OMVPE growth mechanisms. Pyrolysis of TMGa in a radical-gettering toluene environment occurs by a simple radical cleavage mechanism with an activation energy of 59.5 kcal/mol, equal to the strength of the first Ga-CH₃ bond [17]. The activation energy for removal of the second CH₃ radical is less, 35.41 kcal/mol, but the preexponential factor has the anomalously low value of 10⁷.⁹⁴ s⁻¹. The results are nearly the same in He [18], indicating the rate-limiting step in the homogeneous pyrolysis mechanism is the same. In H₂(D₂), the ambient assists pyrolysis slightly, probably owing to H (D) attack of the parent molecule. The major pyrolysis product is CH₄(CH₃D).

RDS can be used to study the heterogeneous pyrolysis of TMGa in situ, in the non-UHV conditions relevant to OMVPE growth [20–22]. TMGa pyrolysis was studied on an As-rich surface, but without the presence of an As precursor. Thus, the results are directly applicable to ALE but may not be directly related to the OMVPE growth mechanism. In addition, the studies are limited to extremely low temperatures of <400°C. Monitoring the signal attributed to Ga dimers during dosing by TMGa at various temperatures suggests that TMGa adsorbs as a molecule. The data are interpreted in terms of TMGa adsorption and subsequent pyrolysis, yielding a desorption energy of 26 kcal/mol and an activation energy for TMGa pyrolysis of 39 kcal/mol. This would give an overall activation energy for growth that would depend on surface coverage, with limiting values of 13 kcal/mol at low surface coverage and 39 kcal/mol at high surface coverages (very low temperatures).

The activation energy of 39 kcal/mol is interpreted in terms of the breaking of the Ga-CH₃ bond; however, this value is similar to the activation energy for methyl radical desorption, as discussed in Section 5.4. It is possible that the formation of Ga dimers is limited by the ability to desorb the methyl radicals covering the surface at low temperatures, as suggested by Kobayashi and Horikoshi.
This interpretation of the data would mean that neither RDS nor SPA gives information about the actual chemical process for TMGa pyrolysis on a GaAs surface. As discussed in Chapter 5, the presence of the H radicals from heterogeneous pyrolysis of the group V precursors may act to remove the CH₃ radicals much more rapidly than simple desorption. In this case, the removal of methyl radicals would be less likely to be the rate-limiting step for the heterogeneous pyrolysis process involved in OMVPE.

ASH₃ pyrolysis is normally heterogeneous. On a GaAs surface, activation energies of 18–23 kcal/mol, obtained using conventional techniques [19, 25], are significantly less than the average As-H bond strength, listed in Table 4.2. The ambient was reported to have no effect. The more recent in situ SPA measurements discussed in Section 5.4.4 yield a similar value of 17 kcal/mol [26].

The pyrolysis process for TMGa and ASH₃ together is radically different. As described in Chapter 5, the pyrolysis temperatures for both are reduced significantly, and the reaction product in D₂ is mainly CH₄, with no deuterated products. The activation energy for the heterogeneous process is reduced dramatically to 15 kcal/mol, a value approximately the same as for the growth process. Equal numbers of Ga and As atoms are removed from the vapor. The joint pyrolysis reaction is clearly not a superposition of the pyrolysis reactions for the individual precursor molecules. The pyrolysis data for InP growth using TMIn and PH₃ are similar, but even more dramatic. The data of Figure 5.28 show that only the PH₃ that can be associated with a TMIn molecule, or perhaps its pyrolysis products, can be pyrolyzed at low temperatures.

These results appear to be directly linked to the growth studies. The activation energy for TMGa + ASH₃ pyrolysis is nearly the same as for the growth process. However, we notice a shift to lower temperatures for the pyrolysis studies. This is a simple consequence of the differences between the two types of experiments. One difference is the higher partial pressures typically used in pyrolysis studies. In addition, the residence time of molecules in the hot zone for the flow-tube apparatus used for pyrolysis studies is measured in seconds. In an atmospheric-pressure OMVPE reactor, the reactants diffuse through the nonuniformly heated region near the substrate in tens of milliseconds. The time that the temperature of the reactants is near the substrate temperature is an order of magnitude less. A ratio of 1,000 in reaction times translates directly into a shift of 100°–150°C on the temperature scale for an activation energy of only 10 kcal/mol. Although perhaps not obvious, this simple analysis applies equally to homogeneous and heterogeneous reactions. This accounts for the enormous differences between the kinetics of atmospheric pressure and UHV (OMMBE) growth to be discussed later.

An analysis of the growth and pyrolysis studies allows the basic growth mechanism postulated in Section 7.1.1 to be tested. The lowering of both pyrolysis temperatures for the combined pyrolysis of TMGa and ASH₃ is explained in terms of
mutual interactions between the adsorbed molecules. The formation of an adduct on the surface between parent molecules, as postulated by Schlyer and Ring [1], is doubtful based on simple chemistry considerations. For the chemisorbed molecules, the empty p orbital for TMGa is occupied in bonding to the electron-rich As atoms on the GaAs surface. Likewise, the lone-pair electrons for AsH₃ interact with the Ga atoms on the GaAs surface. Thus, the bonding that results in adduct formation in the vapor, involving an interaction between the empty p orbital of TMGa and the lone electron pair of AsH₃, will be absent for the same species chemisorbed on the surface. The adduct type of interaction could occur if both source molecules were in a physisorbed state. The pyrolysis data indicate that adsorbed AsH₃ attacks adsorbed TMGa, forming CH₄. It seems feasible that this would lead to the formation of a DMGa-AsH₂ complex, which forms GaAs by eliminating two additional CH₄ molecules. These reactions account for the salient features of the pyrolysis results: formation of CH₄, even in a D₂ ambient, lowering of the pyrolysis temperatures for both TMGa and AsH₃, and the 1:1 ratio of TMGa and AsH₃ pyrolyzed.

An alternate model suggested by the results of Butler et al. [27] and Gaskill et al. [28] is that TMGa pyrolyzes, producing CH₃, that attacks AsH₃, producing AsH₂ and CH₄. These authors found the interaction between CH₃ and AsH₃ to occur homogeneously with the rate constant parameters given in Table 5.1. We could also conceive of the reaction occurring on a surface, as discussed earlier. The adsorbed AsH₂ and DMGa participate in subsequent, rapid heterogeneous pyrolysis steps to form GaAs. This model does not directly explain the lowering of the TMGa pyrolysis temperature when AsH₃ is present, since no radical chain reaction is involved. However, a reduction in the partial pressure of CH₃, due to the interaction with AsH₃, would lead to a decrease in the interaction with DMGa, which would lead to a reduction in the reformation of TMGa [3]. Neither does it explain the reduced pyrolysis temperature when TMGa is replaced by TEGa (or TIBGa), since C₂H₆ (C₄H₉) is produced only in minor concentrations, because of the dominant β-elimination reaction path, and would attack AsH₃ less vigorously than CH₃, since the ethyl (butyl) radical is more stable. Finally, as discussed in Section 5.3.3.1, addition of the CH₃ radical scavenger 1,4-cyclohexadiene (CHD) has no effect on the combined pyrolysis of TMGa and AsH₃, confirming that CH₃ radicals play no dominant role in the pyrolysis reactions.

In summary, consideration of the experimental results for GaAs growth and pyrolysis of various precursors allows a refinement of the model described in Section 7.1.1. To be precise, the adsorption of TMGa and AsH₃ at relatively low temperatures is probably governed by the Freundlich rather than the Langmuir isotherm. The adsorbed molecules interact, giving rapid pyrolysis of both, a 1:1 ratio of AsH₃ and TMGa pyrolyzed, and CH₄ as the major product. At higher temperatures, homogeneous pyrolysis of TMGa produces MMGa, which is adsorbed, and CH₃ radicals, which interact with both AsH₃ and the H₂ ambient, in
the latter case producing H that, in turn, attacks TMGa. The extent to which such homogeneous reactions occur depends critically on the temperature, the concentrations of the precursors, and the reactor geometry and pressure.

A novel approach to increasing the low-temperature growth rate of GaAs is the addition of radicals. Li et al. [29] added tertiarybutyl radicals from the pyrolysis of azo-\(t\)-butane (ATB) to chemically enhance the growth rate of GaAs from TMGa and AsH\(_3\) in H\(_2\). The ATB pyrolyzes at 200°–300°C, yielding \(t\)-butyl radicals and inert molecular nitrogen. At 450°C, the GaAs growth rate was increased by a factor of six. In addition, the surface morphologies were improved. The effect is presumably due to the enhanced homogeneous pyrolysis of the TMGa. Thus, the growth mechanism is actually changed by the addition of \(t\)-butyl radicals to the system.

Another example of the effect of radicals on the growth-rate-limiting step in the growth process is the effect of using TDMASb for the growth of InSb. The low-temperature growth rate is limited by the pyrolysis of the group III precursor, TMIn in this case. Apparently, the N(CH\(_3\))\(_2\) radicals produced during pyrolysis of the Sb precursor attack the TMIn, increasing the pyrolysis rate [30].

### 7.2.2 Low Temperature, Low Pressure

The effect of reducing the reactor pressure by an order of magnitude is clearly seen from the data of Heinecke et al. [6], reproduced as Figure 7.4 for the growth of GaAs using TMGa and AsH\(_3\). As for growth at atmospheric pressure, the low-pressure (76 Torr or 10\(^4\) Pa) growth rate versus temperature behavior can be broken into three regions, with growth rate increasing with temperature for

![Figure 7.4](image-url)
$T < 550^\circ C$, nearly temperature-independent over the temperature range normally used for OMVPE, and with a hint of a decrease in growth rate with increasing temperature in the highest-temperature regime.

In the low-temperature, surface kinetically limited growth regime, the reaction rate appears to be nearly independent of total pressure in the reactor. A slight orientation dependence of growth rate is observed, similar to the results of Reep and Ghandhi at atmospheric pressure. The activation energy is approximately 25–31 kcal/mol, slightly higher than for the atmospheric pressure case discussed in the last section.

These results are all consistent with the L-H growth model for low temperatures postulated in Section 7.1.1, as indicated in Table 7.1. In the low-temperature, kinetically limited regime, the growth rate is expected to be independent of reactor pressure, provided the reactant partial pressures are constant, dependent on the substrate orientation, and independent of flow velocity. The growth rate dependence in the midtemperature regime will be discussed in Section 7.3.

Heinecke et al. also report the effects of reactant pressures on the growth rate at both low and atmospheric pressures in the kinetically limited temperature range. The AsH$_3$ flow rate was found to have no effect on the growth rate over the pressure range studied, with AsH$_3$ pressures greater than the TMGa pressure. This is similar to the results of Reep and Ghandhi [2] at atmospheric pressure. The effect of TMGa pressure is seen in Figure 7.5. A linear increase in growth rate with increasing TMGa pressure is observed at low partial pressures, followed by a saturation region. In terms of our discussion in the last section, this is attributed to the saturation of special sites on the surface. The data indicate that neither the flow velocity nor the reactor pressure affect growth rate in the linear regime. From Figure 7.4, we see that all this data is in the kinetically limited regime; thus, an increase in temperature leads to an increase in growth rate.

![Figure 7.5](diagram.png)

**Figure 7.5.** Dependence of GaAs growth rate using TMGa and AsH$_3$ on TMGa pressure for various growth conditions. (After Heinecke et al. [6], reprinted with permission from Journal of Electronics, a publication of the Metallurgical Society, Warrendale, Pennsylvania.)
Less easily understood is the obvious, but small, dependence of growth rate on total pressure and gas velocity: this is unexpected for growth in the kinetically limited regime. Heinecke et al. explained the phenomena in terms of desorption or diffusion of products away from the interface. Neither explanation is appealing. If desorption were the rate-limiting step, the saturation would be independent of both total pressure and flow velocity. If diffusion of products away from the interface were rate limiting, the growth rate would not be thermally activated. An explanation consistent with the model proposed here is simply that at 510°C, both mass transport and surface reaction rates play a role in determining the growth rate. In terms of Figure 2.29, $\Delta \mu_{\text{p}}$, is not negligible in comparison with $\Delta \mu_{\text{s}}$. The total pressure and flow velocity affect the mass transport and hence the growth rate even though the growth rate increases nearly exponentially with temperature.

As expected from the simple paradigm developed in the last section, the growth mechanism dominant at low temperatures is largely unaffected by an order of magnitude decrease in the total reactor pressure. This is the growth regime normally known as low pressure, or LP-OMVPE.

### 7.2.3 Low Temperature, Very Low Pressure

Results are scarce for OMVPE growth at even lower pressures, between 0.1 and 10 Torr. The primary advantage of using these very low pressures is the ease of local or selective epitaxy where epitaxial layers are deposited only in the openings in dielectric masks deposited on the III/V substrate [31, 32]. This capability is not available for MBE using conventional elemental sources. For MBE, polycrystalline growth on the dielectric mask is nearly inevitable since the nonvolatile elemental group III atoms cannot leave the surface at normal growth temperatures. In conventional OMVPE, with reactor pressures of 76–760 Torr, pyrolysis of very labile precursors may also result in nonvolatile species adsorbed on the growing surface. However, for most common group III precursors, selective growth is possible even at atmospheric pressure. In terms of the simple model developed earlier, selective growth is dependent on preventing the adsorption of either of the reactants on the masked surface. The growth process occurs via surface interactions; thus, the absence of one of the species is sufficient to prevent growth. For example, the lack of AsH₃, which is perhaps least likely to adsorb on a masked surface, will retard the heterogeneous pyrolysis of TMGa. Thus, even the deposition of a Ga layer would be prevented by the absence of adsorbed AsH₃.

This mechanism apparently explains the experimental results reported by Heinecke et al. [32]. They observed selective growth even at reactor pressures as high as 76–760 Torr, provided that the temperature was greater than 700°C. This means that the TMGa pyrolysis is not complete. This may be partially due to the lack of AsH₃ adsorption on the masked surface. In addition, since we expect the TMGa to be partially pyrolyzed homogeneously, during diffusion through the
boundary layer. MMGa must not be strongly adsorbed on the masked surface at these temperatures, otherwise Ga droplets would be formed. Using TEGa as the group III source resulted in the virtual inability to effect selective epitaxy. In this case, TEGa decomposes rapidly, resulting in a nonvolatile product, as evidenced by the rapid low-temperature growth rate observed in Figure 7.3. The presence of Ga on the surface may result in the adsorption and pyrolysis of AsH$_3$, giving rise to GaAs, rather than Ga deposition.

Heinecke et al. [32] observed selectivity at temperatures greater than 620°C for TMGa and AsH$_3$ at a reduced pressure of 500 Pa. At lower pressures, in the OMMBE regime, selectivity was obtained over the entire temperature range studied, from 525°C to 635°C. Naturally, reduced pressure growth favors selective growth since the homogeneous pyrolysis of TMGa and the adsorption of both AsH$_3$ and TMGa are retarded.

In contrast with the higher pressure results described in the last section, at very low system pressures the growth rate becomes dependent on the AsH$_3$ partial pressure even though it is much greater than the TMGa pressure, as seen in Figure 7.6. In fact, in a vacuum growth system, no growth takes place using TMGa and AsH$_3$ [33] unless the AsH$_3$ is precracked. In this case, where no gas-phase collisions occur, undecomposed, room-temperature TMGa and AsH$_3$ are the species reaching the surface. Neither can apparently pyrolyze in the brief time before being desorbed. Cracking the AsH$_3$ produces more strongly adsorbed elemental As and As$_2$ that react with TMGa (or more commonly TEGa) on the surface during OMMBE (or CBE) growth [34]. These techniques will be discussed more fully in the next section.
The absence of GaAs growth using TMGa and AsH₃ in UHV conditions has led to the suggestion that the growth processes are limited by gas-phase interactions [7]. A more likely explanation is related to the very low AsH₃ partial pressure at the solid/vapor interface during OMVPE growth. In the extreme case where UHV conditions exist at the solid surface, each AsH₃ molecule has only one chance to adsorb and decompose. After desorption it rapidly diffuses away. For the relatively high AsH₃ pressures of approximately 10⁻¹⁻¹⁻² Torr for OMVPE growth at reactor pressures of 76 to 760 Torr, each AsH₃ molecule will impinge on the surface a large number of times before being swept away. Thus, the probability of AsH₃ pyrolysis is much higher.

A sufficiently large reduction of total pressure makes mass transport processes so rapid that kinetically limited growth is observed even at temperatures as high as 650°C. This is demonstrated by the pressure independence of growth rate for pressures of less than 10⁻¹⁻¹⁻² Torr shown in Figure 7.7. An additional interesting result obtained by Heinecke et al. [33] is that the surface-reaction-limited growth rate becomes dependent on total pressure at very low pressures, even when the partial pressures are fixed, as seen in Figure 7.8. These results are ascribed to a decrease in gas-phase interactions at low system pressures. However, since the individual partial pressures remain constant as the system pressure is reduced, this explanation is not entirely satisfactory. More likely, this is the effect of a decreased heterogeneous AsH₃ pyrolysis rate, as described earlier, with a concomitant increase in TMGa desorption before pyrolysis can occur, resulting in a lower growth rate. At low temperatures, below 427°C, and low reactor pressures of 500 Pa, the growth virtually stops using TMGa and uncracked AsH₃. The growth increases markedly if the process is stimulated using a plasma [33]. The growth process is presumably changed in this case to a mechanism resembling the OMMBE process.

![Figure 7.7](image_url)
using precracked AsH₃, as described previously and in the next section. The use of low pressures and low temperatures allows for the possibility of selective growth using laser stimulation [35].

Heinecke et al. [33] considered the effect of the plasma to be possibly due to the creation of atomic hydrogen. This active radical might be expected to play a role in both the growth kinetics and in carbon incorporation, which is high in layers grown under these conditions. However, a pure H₂ plasma was found to have no effect on either growth rate or carbon incorporation.

A few kinetic studies in the very low-pressure region yield more information about the reaction mechanisms. Horiguchi et al. [36] investigated mass-spectrometrically the growth of GaAs in a vertical reactor using TMGa or TEGa and AsH₃ in the pressure range from 0.05 to 100 Torr, at 650°C, with a constant reactor input giving a V/III ratio of 20. For pressures of 1 Torr and below, they found the TMGa to decompose by sequential radical elimination. This is expected at these low pressures where gas-phase interactions are minimized. In particular, the attack of TMGa by H radicals generated by CH₃ interactions with the H₂ ambient, described in Section 5.3.1.2, would play no role. At higher reactor pressures, approaching 10 Torr, Horiguchi et al. considered the CH₃ radicals to react mainly with the H₂ ambient, producing CH₄. Another possibility, not discussed by the authors, is that the CH₃ radicals interact with AsH₃, also producing CH₄.

Figure 7.8. Temperature dependence of GaAs growth rate using TMGa and AsH₃ at two reactor pressures: 10⁴ and 500 Pa. (After Heinecke et al. [33], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
At lower pressures the concentration of methylarsine species was found to increase to become a substantial fraction of the CH$_4$ produced. This can be rationalized in terms of the postulated reaction mechanism. At very low precursor partial pressures, the surface concentrations of TMGa and AsH$_3$ will be small. This will decrease TMGa-AsH$_3$ interactions, leading to the independent pyrolysis of the precursors. Reactions of partially decomposed AsH$_3$ radicals (AsH and AsH$_2$) with CH$_3$ from TMGa pyrolysis would lead to the formation of the methylarsines, some of which would be desorbed. The high CH$_3$ concentrations on the surface under these conditions would lead to extremely high carbon levels in films grown at very low pressures using TMGa.

The results using TEGa and AsH$_3$ indicate that the homogeneous pyrolysis of TEGa proceeds mainly via the $\beta$-elimination reaction, producing mostly C$_2$H$_4$ at reactor pressures of 10 Torr and above. At lower reactor pressures, down to 0.1 Torr, the concentration of ethylarsine increases markedly, as seen in Figure 7.9. This is an indication that TEGa pyrolyzes by the radical mechanism on the GaAs surface where the $\beta$-elimination reaction is blocked because the empty p orbital is occupied by the bond formed to the surface atom in agreement with the results discussed in Chapter 5. Since the ethylarsines are produced mainly at the lowest pressures, the reaction between AsH$_3$ and the ethyl radicals must be heterogeneous.

![Figure 7.9. Reactor pressure dependence of mass-spectrometer peak intensities for the TEGa-AsH$_3$ system. (After Horiguchi et al. [36].)](image)
Carbon incorporation is greatly reduced in very low-pressure OMVPE by substituting TEGa for TMGa. The reduction of reactive radicals by using TEGa has long been known to reduce carbon incorporation in GaAs grown at higher reactor pressures, as discussed in Section 7.3. However, at very low pressures, the presence of ethyl radicals on the surface leads to increased carbon incorporation even using TEGa. This is a significant problem for very low-pressure OMVPE and especially for OMMBE and CBE.

7.2.4 High Vacuum

To complete our discussion of the kinetically limited growth regime, we now move to a discussion of OMMBE (or CBE). At very low pressures of less than $5 \times 10^{-4}$ Torr, mass transport proceeds via molecular flow with no collisions in the gas phase [37]. This means that no homogeneous pyrolysis can occur, since the molecules are cool when they reach the substrate. As we will see, using precracked AsH$_3$ and TMGa at high temperatures, the heterogeneous pyrolysis is rapid, so the growth rate is limited by the group III flux to the surface. At lower temperatures the growth process is kinetically limited, although the purely heterogeneous kinetics appear to be quite different than at the higher pressures used in conventional OMVPE growth.

Putz et al. [38] studied the pyrolysis of both TMGa and TEGa in the cracking tube of an OMMBE apparatus. At temperatures above 375°C, TMGa begins to pyrolyze by stepwise elimination of CH$_3$ radicals. TEGa pyrolysis begins at about 50°C lower temperatures. Evidently the homogeneous pyrolysis mechanism is $\beta$ elimination, since the major product is ethene, C$_2$H$_4$. This is in complete agreement with the results presented in Chapter 5.

TMGa is found to give extremely high carbon concentrations, up to $10^{20}$ cm$^{-3}$, in GaAs layers grown by OMMBE [38], presumably because of the CH$_3$ radicals on the surface. The AsH$_3$ must be precracked, thus eliminating the source of H radicals necessary to form CH$_4$, which is rapidly desorbed. Carbon doping is not always undesirable. As discussed in Section 8.1.6, extremely high p-type doping levels can be obtained using carbon, which is desirable for some device structures. TEGa gives significantly lower carbon doping levels, between $10^{14}$ and $10^{16}$ cm$^{-3}$, so is most commonly used for OMMBE growth. Low TEGa fluxes yield n-type layers, with 77° K mobilities as high as 72,000 cm$^2$/Vs.

The OMMBE growth rate is linearly dependent on the TMGa or TEGa flux for normal growth conditions [34, 38]. No growth occurs using TMGa unless the AsH$_3$ is precracked, apparently because the unpyrolyzed TMGa will not adsorb and pyrolyze heterogeneously on the (4 × 2) surface formed unless As is present, as discussed earlier. The dependence of growth rate on As flux is telling. For TEGa, a reduction of the flux below a critical value results in liquid Ga deposition.
and whisker growth, similar to the situation in atmospheric-pressure OMVPE growth using TMGₐ and AsH₃, indicating that TEGa adsorbs and pyrolyzes at the surface even in the absence of AsH₃. This situation is clearly described by the phase diagram of Figure 2.11. However, using TMGa, the growth rate decreases smoothly with reduced As flux below the critical value where the As flux equals the Ga flux. The growth rate decreases to zero with decreasing As flux with little metallic Ga deposition. Heterogeneous TMGa pyrolysis is apparently dependent on having adsorbed As on the surface (i.e., formation of a favorable reconstruction). This is basically the mechanism leading to selective epitaxy, as discussed previously, and ALE, discussed in Chapter 9.

The temperature dependence of growth rate using TMGa and AsH₃ sources is shown in Figure 7.10. At temperatures below approximately 570°C, the growth rate increases exponentially with increasing temperature, indicating a kinetic limitation to the growth process. The activation energy is measured to be 22 kcal/mol. This value is similar to those obtained at higher reactor pressures using precracked AsH₃ and As sources that pyrolyze independently at temperatures lower than for TMGa. In the midtemperature range, the growth rate is independent of temperature. This appears to be similar to the mass-transport-limited growth regime described for atmospheric-pressure OMVPE except that mass transport is by molecular flow in this case. In the following sections, the result of more sophisticated characterization and modeling techniques will be summarized for TEGa and TMGa separately.

Figure 7.10. GaAs growth rate versus deposition temperature for OMMBE growth using TMGa and AsH₃. Z is the fraction of AsH₃ prepyrolyzed. (After Pütz et al. [38], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
7.2.4.1 CBE Growth Studies Using TEGa

Robertson et al. [34] suggested the first detailed model of the processes occurring during CBE growth of GaAs from TEGa and cracked arsine using the experimental growth rate versus temperature behavior plus intuitive ideas about the important species and processes. Since then, the basic model has been refined using the results of fundamental surface science experiments, including the “static” experiments described in Chapter 3 such as TPD. The approach here will be to describe the refined model of French and Foord [39] (termed the FF model in what follows), including a discussion of the growth rate versus operating parameters such as Ga and As fluxes as well as temperature. In addition, the results of the surface science experiments are included. The results of “dynamic” modulated beam mass spectroscopy (MBMS) studies were also used to guide the selection of rate constants in the model. These experiments are conducted during growth, thus overcoming many of the disadvantages of the “static” experiments described in Chapter 5. Use of the MBMS technique also avoids discrimination problems encountered in normal mass spectroscopy studies [40–42].

Robertson et al. [34] suggested that at low temperatures, heterogeneous pyrolysis of TEGa limited the growth rate. However, MBMS experiments by Martin and Whitehouse [41] and others clearly show that TEGa pyrolyzes rapidly to produce DEGa at much lower temperatures. Murrell et al. [43] performed detailed experimental (LEED, XPS, Auger spectroscopy, high-resolution EELS [electron energy loss spectroscopy], and TPD) analysis of the surface processes occurring during the CBE growth of GaAs using TEGa. The XPS data clearly indicate that TEGa is chemically bonded to the GaAs surface. TEGa is a Lewis acceptor that is chemisorbed to the GaAs surface by the donation of electrons from the surface into the vacant p orbital of the TEGa. This is contrary to speculation [44] that such a process would be sterically hindered for the planar TEGa molecule. Robertson et al. [34] assumed a physisorbed state for the TEGa with a consequently lower activation energy for desorption than measured experimentally.

The results of Murrell et al. [43] indicate that TEGa pyrolysis is not the rate-limiting step for low-temperature growth. Site blocking by adsorbed ethyl radicals was found to be the limiting factor at temperatures of under 350°C, where the sharply increasing growth rate with increasing temperature is due to the rate-limiting step of ethyl radical decomposition to adsorbed H and ethene. Ethene is rapidly desorbed from the surface as is H, as molecular H2. The kinetic parameters for these processes were obtained from TPD studies [39, 43]. The resulting temperature dependence of growth rate is shown in Figure 7.11. In this low-temperature regime the GaAs growth rate is also observed to decrease with increasing arsenic flux. This is attributed to blocking of the surface sites by adsorbed arsenic in the FF model. The surface was modeled as a square lattice with
Design of the OMVPE Process

Figure 7.11. CBE growth rate of GaAs versus temperature for various TEGa flow rates. The curves were calculated by French and Foord [39]. The experimental data are from Robertson et al. [34]. (After French and Foord [39], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)

competitive adsorption of the various species (TEGa, DEGa, C₂H₅, As, and H) on the same sites. The larger radicals would be expected to occupy more space on the surface, owing to steric effects. Thus, the model includes lateral repulsion between adsorbed DEGa species using a quasi-chemical thermodynamic model. This part of the model is essential to fit the TPD data but has little effect on the calculated growth rates.

The GaAs growth rate versus temperature exhibits a maximum, as seen in Figure 7.11. This is due to a competition between desorption and decomposition of DEGa. Of course, only decomposition leads to growth. This was a salient feature of the model of Robertson et al. [34]. However, direct evidence of DEGa desorption was first obtained by Martin and Whitehouse in their MBMS studies [41]. At temperatures above 660°C, the growth rate drops rapidly due to elemental Ga desorption.

The increase in carbon incorporation at higher growth temperatures was attributed by Robertson et al. [34] to the activation energy for carbon incorporation, presumably due to pyrolysis of the ethyl radicals, being larger than the 30 kcal/mol activation energy estimated for desorption of ethyl radicals.

Small amounts of In (2%) were found to drastically reduce the growth rate of GaAs above 500°C [41]. The source of the In, either TEIn or metallic In, was found to be immaterial [45]. This was interpreted in terms of increased desorption of DEGa when bonded to surface In atoms. A small concentration of In has a large effect because the In is segregated to the surface [46]. This phenomenon causes practical problems for control of the composition of GaInAs alloys by CBE. An
interesting possibility for solving this control problem is to design appropriate new precursor molecules that avoid the production of DEGa species on the surface. Perhaps, as suggested by Foord et al. [47], trimethylamine-gallane and related molecules would be suitable. As discussed in Chapter 4, such molecules are only marginally stable, so they may have practical disadvantages.

FitzGerald et al. [48] reported that the effect of Al was opposite to that of In: the presence of Al in the solid suppressed the desorption of both TEGa and DEGa. Their results indicate that Al modifies the surface chemistry resulting in incorporation of carbon into the layer. They concluded that C contamination problems in Al-containing semiconductors grown by CBE will be solved only when carbon-free precursors are developed for all group III precursors. This is consistent with the notion that different precursors will be required for CBE than for OMVPE [49].

An advantage of considering the kinetics in the UHV OMMBE or CBE process is obviously the ability to view the surface using various analytic techniques. For example, Robertson et al. [34] observed that the steady-state coverage of the alkyl species was small, since no degradation of the RHEED pattern was observed relative to the static no-growth condition. The surface coverages of DEGa and ethyl radicals were estimated to be \(< 10^{-5}\) monolayers during high-temperature growth. This point is consistent with earlier discussions (e.g., see Chapter 3) indicating that the growth of high-quality epitaxial layers depends on the adsorbed radicals or atoms having sufficient time and mobility to find the low-energy sites, presumably kinks and ledges on the surface, and it supports the idea that the saturation of growth rate at 500°C, discussed in Section 7.1.1, is due to saturation of special growth sites on the surface. Only at very low temperatures of 350°C, where the growth is virtually stopped, is the surface coverage observed to be large. As another example, Foord et al. [50] were able to clearly demonstrate that for GaSb growth by CBE on (001) surfaces, the rate of heterogeneous TEGa pyrolysis was strongly dependent on the surface reconstruction. The TEGa decomposition rate was found to be far greater on \((1 \times 3)\) than on \(c(2 \times 6)\) surfaces.

### 7.2.4.2 CBE Growth Studies Using TMGa

Foxon, Joyce, and coworkers [44, 51, 52] used MBMS to study the OMMBE growth of GaAs using TMGa and elemental As. They report a complex temperature dependence of growth rate, with a rapidly increasing growth rate at low temperatures, a peak at about 500°C, a slight dip and a second increase at temperatures above 600°C, as seen in Figure 7.1. The MBMS results were interpreted in terms of dissociative chemisorption of TMGa, in agreement with the static surface studies, discussed in Chapter 5, where decomposition of TMGa was observed using TPD at temperatures below 350°C. The complex temperature dependence of growth rate was attributed not to bond breaking in the TMGa molecule but
to site blocking by two stable surface species. At low temperatures the activation energy is 38.6 kcal/mol [52], nearly equal to that determined from the low-temperature pyrolysis studies using SPA discussed earlier.

Kaneko et al. [53] studied the OMMBE growth of GaAs from TMGa and elemental As using RHEED oscillations to monitor the growth process. The surface was seen to have a (2 × 4) reconstruction during growth. At low temperatures, the rapid increase in growth rate with increasing temperature, with an activation energy of 39 kcal/mol, was thought to be limited by the desorption of methyl radicals from the surface; thus, CH₃ is believed to be one of the site-blocking species mentioned earlier. The activation energy is in rough agreement with the values measured directly for CH₃ desorption. Of course, the concentration of CH₃ on the surface, the surface reconstruction, and the presence of other species on the surface may all have an effect on the activation energy for desorption. As already mentioned here and in Chapter 5, it is dangerous to attempt to directly link the results of static and dynamic experiments. The second site-blocking species responsible for the dip in growth rate at higher temperatures is thought to be excess As.

A comparison of nominally (001) substrates misoriented by a few degrees in the A and B directions indicates an anisotropy of Ga incorporation at the two types of step edges, suggested to be due to differences in the rates of MMGa decomposition at the two step types. A mechanism based on CH₃ site blocking at the step edge was suggested.

Isu et al. [54] observed a similar complex dependence of growth rate on substrate temperature, with "two humps." A mass-spectrometric analysis of the dependence of the desorption of methylgallium species for (001) GaAs showed that the pyrolysis of TMGa is strongly affected by the presence of elemental As supplied simultaneously. Without As, only TMGa was desorbed. On a bare, As-stabilized surface, DMGa and/or MMGa were desorbed. This is an important observation, since it indicates once again that the pyrolysis mechanism determined using UHV surface science techniques will not necessarily give mechanistic information important for understanding either CBE or OMVPE growth, since the surface reconstruction is likely to be different for each set of experimental conditions. In fact, it is probably not valid to assume that the rate limiting step for GaAs growth at low temperatures determined for OMMBE conditions will be the same as for the OMVPE process because the surface reconstruction is likely (2 × 4) for CBE and (4 × 4) for OMVPE. Nevertheless, the results of both static and dynamic UHV experiments offer insights that are helpful in attempting to unravel the complex OMVPE process where fewer analytic tools are available.

RHEED studies have been extremely valuable for understanding the UHV processes, MBE, OMMBE, and CBE. However, attenuation of the electron beam by the atmosphere precludes the use of this technique for the study of OMVPE growth. An equivalent technique is the use of grazing incidence X-ray scattering (GIXS) [55]. However, this requires an extremely bright X-ray source, namely a
For this reason, GIXS will never be a widely used technique. Nevertheless, a collaborative effort between IBM, AT&T Bell Laboratories, and the Stanford Synchrotron Radiation Laboratory has produced a set of data for the growth of GaAs using TMGa (or TEGa) and TBAs in a low-pressure (60-Torr) OMVPE reactor that reveal important aspects of the OMVPE growth process. The technique allows the in situ determination of certain features of the growth process, similar to the RHEED technique discussed in Chapter 3. For example, using typical OMVPE growth conditions, the surface reconstruction during growth on (001) GaAs substrates was found to be (4 $\times$ 4), although other reconstructions such as (2 $\times$ 4) and (4 $\times$ 2) could be produced by reducing the As partial pressure [56]. The typical reconstruction during MBE growth is (2 $\times$ 4). The (4 $\times$ 4) reconstruction during OMVPE growth is presumably due to the higher As pressure during growth as indicated by the phase diagram (see Figures 2.50 and 3.4). The length scale for two-dimensional island nucleation can also be determined. The relatively large sizes observed led Tersoff et al. [57] to the conclusion that the surface processes occurring during OMVPE can be validly treated using near-equilibrium models.

An important observation of these studies was that GIXS oscillations corresponding to the layer-by-layer growth cycle [55] correlate closely with RDS oscillations observed simultaneously during OMVPE growth. This validates many features of the optical techniques for determining the growth rate in situ as well as for determination of the surface reconstruction during growth [56].

The results of mass-spectroscopy studies in an ersatz reactor, discussed in Section 5.3.3, can also be used to give insights into the heterogeneous copyrolysis of a group III and a group V precursor during the OMVPE growth process. As an example, Larsen et al. [18] studied the pyrolysis of TMGa and AsH$_3$, the most common combination of precursors used for the OMVPE growth of GaAs. The heterogeneous pyrolysis of AsH$_3$, alone, on a GaAs surface was found to have an activation energy of 23.2 kcal/mol [19]. The heterogeneous pyrolysis of TMGa, alone, on a GaAs surface cannot be studied by these techniques, since Ga covers the GaAs surface without the simultaneous presence of AsH$_3$. For TMGa and AsH$_3$ together, Larsen et al. [18] found the low temperature pyrolysis to occur with an activation energy of 34.7 kcal/mol. The two pyrolysis reactions were concerted at low temperatures, in the sense that one molecule of arsine was pyrolyzed for each molecule of TMGa and the product was CH$_4$, even in a D$_2$ ambient. This indicates that one CH$_3$ radical from TMGa combines directly with one H ligand from AsH$_3$ to produce the molecule of methane.

These results imply that the rate-limiting step in the low-temperature OMVPE growth of GaAs from these two precursors is the joint pyrolysis rate. This result differs from that inferred from the OMMBE results discussed here—that the desorption of CH$_3$ from the surface sites required for adsorption and subsequent decomposition of TMGa limits the low-temperature growth rate. However, when a high concentration of atomic H, from the heterogeneous pyrolysis of AsH$_3$, is
present during OMVPE growth, it is perhaps not surprising that formation of CH₄, which is immediately desorbed, is more rapid than direct CH₃ desorption. A mathematical model developed by Windeler and Hicks [58] supports this conclusion. They found that the formation of CH₄ from the TMGa and AsH₃ and subsequent desorption occur more rapidly than CH₃ desorption, using the kinetic data from the extensive static UHV studies described briefly earlier.

Of course, this method for the rapid removal of methyl radicals from the surface will make another step in the overall reaction rate limiting. Although the data are not definitive, a strong possibility is that the heterogeneous TMGa pyrolysis rate limits the low-temperature OMVPE growth rate. This appears to be in general agreement with the correspondence between the low-temperature limit for pyrolysis of various Ga and Al precursors and the low-temperature limit for the onset of epitaxial growth, discussed earlier here and in Chapter 5. However, care must be exercised in interpreting these results since it is possible that the pyrolysis rate is limited by the ability to desorb radicals blocking the sites necessary for heterogeneous pyrolysis of the group III precursors. A similar correlation has also been noted between the low-temperature growth rates of GaAs using TMGa, TEGa, and TIBGa [59], as described previously and shown in Figure 7.3. The increasing low-temperature growth rate has been correlated with the decreasing Ga-R bond strength. However, the surface-R bond strength will probably decrease in qualitatively the same manner.

### 7.2.4.3 CBE Growth Studies Using Other Ga Precursors

Without the presence of atomic H on the growing surface, alkyl groups from pyrolysis of the group III precursors give relatively high levels of carbon contamination in GaAs and, especially, AlGaAs grown by CBE. The new family of alane-adduct precursors has reduced this problem significantly. However, the related gallane-adduct precursors are too unstable for convenient use. This has resulted in the study of tritertiarybutyl- and triisopropyl-gallium (TTBGa and TIBGa, respectively) [60, 61]. TIBGa gives high growth rates and low values of carbon contamination, due either to the low reactivity of isobutyl radicals or to pyrolysis by β-elimination reactions, as discussed in Section 5.4.4.3. Because of steric effects, TTBGa gives low growth rates of less than 0.05 µm/h. The Ga is surrounded by three bulky tertiarybutyl ligands, preventing it from sticking to the (001) GaAs surface.

### 7.2.5 Summary of Kinetically Limited OMVPE Growth

It is worthwhile to pause at this point to see whether an examination of the combined results in the various pressure regimes, summarized in Table 7.1, allows
an elaboration of the model of the reactions occurring during low-temperature OMVPE growth presented in Section 7.1.1. For clarity, only results using TMGa and AsH₃ will be considered in this section.

The seemingly simplest case is the growth of GaAs in a high-vacuum environment (i.e., OMMBE and CBE) where no gas-phase interactions can occur. The result is spectacularly simple: no growth occurs without precracking the AsH₃. At very low reactant partial pressures, the surface coverages of both TMGa and AsH₃ are extremely small. This essentially stops pyrolysis and growth since heterogeneous pyrolysis rates are proportional to the surface coverage, as discussed in Section 3.4. The CBE process involves adsorption of As and As₂ from the precracked AsH₃. Since As₂ and especially As will be much more strongly adsorbed than AsH₃, this takes care of the As needed for GaAs growth. Apparently, the atomic As adsorbed on the surface also induces adsorption and subsequent pyrolysis of TMGa. However, the low-temperature growth rate appears to be limited by CH₃ desorption with an activation energy of approximately 38.6 kcal/mol.

As the reactor pressure is increased to the 0.1–10 Torr range, growth occurs without precracking but is dependent on the AsH₃ flow rate and is increased by cracking the AsH₃ using a plasma. The key to understanding the growth process in this pressure regime is the increased formation of methylarsines as the pressure is reduced from 10 to 1 Torr. The surface coverages of TMGa and AsH₃ are clearly large enough to allow pyrolysis and growth of GaAs at reasonable rates. However, the surface coverages are still so low that TMGa-AsH₃ interactions on the surface are precluded. The independent pyrolysis of the precursors produces AsH, AsH₂, and CH₄, which combine to form the methylarsines observed. The activation energy for growth in this pressure range is approximately 23 kcal/mol.

For conventional OMVPE, in the pressure range from 76 to 760 Torr, surface coverages are relatively high, which encourages TMGa-AsH₃ interactions. This results in the main product becoming CH₄ as well as the other pyrolysis and growth results summarized near the end of Section 7.2.1. This also gives rise to the low activation energies of approximately 11–19 kcal/mol, depending on the surface coverage and substrate orientation. When rapidly pyrolyzing As sources or precracked As is used, the activation energy reverts to the higher value observed for very low-pressure OMVPE where TMGa pyrolysis is stimulated by adsorbed As rather than by AsH₃.

The rapid growth rate at low temperatures and the low activation energy for atmospheric-pressure OMVPE using TMGa indicate that methyl radical desorption is not the rate-limiting step, probably because the atomic hydrogen produced during pyrolysis of the As precursor leads to rapid methane formation and desorption. Thus, the rate-limiting step might be the actual rate of TMGa pyrolysis on the GaAs surface, assisted by the presence of arsine. A second-order process would be consistent with the relatively small preexponential factor inferred from a comparison of the OMVPE and CBE growth rate data in Figure 7.1.
7.3 Midtemperature, All Pressures

In the midtemperature region, where the growth rate is nearly temperature-independent, the growth rate is generally limited by mass transport for all of the pressure regimes, as indicated in Table 7.1; thus, kinetic information concerning the reaction mechanisms cannot be obtained from the growth rate versus temperature and reactant flow rate experiments. Of course, for growth in the high-vacuum regime, surface science and MBMS studies give information about the reactions occurring on the surface. For the conventional OMVPE-pressure regime, information concerning both thermodynamics and kinetics can be indirectly obtained by considering the effects of growth parameter variations on dopant incorporation. First, however, let us consider the mass-transport process in some detail.

This section covers all pressure regimes for the simple reason that pressure is one of the main variables in the mass transport processes. In this regime, the growth rate from the simple boundary layer model can accurately be considered to be given by the equation [6, 62]

\[ r_g = \text{(constant)} P_{\text{TMGa}} \left( \frac{v}{P} \right)^{1/2} \]

where \( P_{\text{TMGa}} \) is the absolute pressure of TMGa in the input gas stream, since it is considered to be completely depleted at the interface, \( u \) is the gas velocity, and \( P \) is the total system pressure. This behavior is seen in Figure 7.4. As the pressure is decreased by an order of magnitude at constant flow velocity and TMGa pressure, the growth rate increases by a factor of \((10)^{1/2}\). Similarly, as the flow velocity is increased with other parameters constant, the growth rate increases. This is shown more clearly in Figure 7.12 where growth rate is plotted versus \( v^{1/2} \). The agreement between the data and the simple model fails at low velocities and low pressures because the boundary layer thickness becomes comparable to the reactor height. In this regime, the growth rate is also found to be independent of substrate orientation [63]. This is a further indication that the growth rate is mass transport controlled. Aspnes et al. [4] offered an alternative explanation of the nearly temperature-independent growth rate of GaAs using TMGa and AsH₃ at atmospheric pressure in the midtemperature range. Based on their low-temperature, \textit{in situ} RDS results, they suggest that the growth is controlled by TMGa adsorption, desorption, and heterogeneous pyrolysis over the entire temperature range from 300° to 750°C.

The resolution of this disagreement is a good example of the value of a simple model for the overall growth process as well as the importance of examining the growth process from diverse viewpoints. As the results of Aspnes et al. illustrate, a temperature-independent growth rate is not sufficient to establish unambiguously the process as being mass transport limited. For surface-kinetically limited
growth, the rate cannot be a function of gas velocity and is expected to be strongly dependent on substrate orientation. Since the growth rate is observed to be independent of substrate orientation and to increase as $v^{1/2}$, the growth rate simply cannot be controlled by TMGa surface reactions. It is clearly mass transport limited.

Several reports of the effect of total reactor pressure are found in the literature. Kuech et al. [64] found that with a constant input molar flow rate of all constituents, the growth rate for GaAs using TEGa and AsH$_3$ increased by approximately 25% when the reactor pressure was increased from 20 to 76 Torr. They stated that the same behavior was observed using TMGa and AsH$_3$. Kimura et al. [65] found the opposite dependence. The growth rate increased as the pressure was decreased from 20 to 2 Torr, possibly outside the regime of the boundary layer model. Clawson and Elder [66] report a similar result for InP grown using TMIn and PH$_3$: as the pressure was increased from approximately 10 to 760 Torr, the growth rate was found to decrease by a factor of 2.5. In each of these experiments the input flow rates were constant. Thus, the partial pressure of the group III reactant is inversely proportional to the total reactor pressure. The gas velocity is also inversely proportional to the total pressure. From Equation (7.1), the growth rate should be independent of the reactor pressure. This is also consistent with the results in Figure 1.1, where the growth efficiency is seen to be essentially the same at 76 and 760 Torr.

The results of in situ growth rate studies using GIXS for GaAs grown using TMGa and TBAs are shown in Figure 7.13. The pressure was reduced from 150 to 20 Torr while maintaining a constant TMGa flow rate into the reactor. In the
range from 40 to 150 Torr, the pressure has no effect, as suggested by the prior analysis. By 20 Torr, there is a 30% reduction. Increasing the TBAs flow rate by 4× restores the higher growth rate measured for higher reactor pressures. These results were interpreted as due to the increasing importance of heterogeneous processes at low reactor pressures.

We now move to a discussion of what can be learned about the kinetic and thermodynamic aspects of growth in the mass-transport-limited regime. From previous discussions (Chapter 2), the effects of increasing temperature on dopant incorporation are known to depend on the nature of both the dopant element and the precursor molecule. The distribution coefficients for volatile dopants such as Zn, S, Se, and Te tend to decrease with increasing temperature for thermodynamic reasons. The opposite behavior is found for stable dopant molecules such as SiH₄ and SnH₄. In this case, the pyrolysis rate limits dopant incorporation, so the effective distribution coefficient is kinetically limited. For the nonvolatile elements, an increased growth rate is expected to decrease the impurity level, since the impurity flux is fixed while the host flux is increased. In other words, the impurities become more dilute in the solid. These thermodynamic and kinetic effects are entirely consistent with the growth model.

The effect of V/III ratio on the incorporation of intentional dopants, described in Chapter 2, clearly indicates the importance of thermodynamic effects in the regime of growth parameters where mass transport controls the growth rate. The concentrations of volatile dopants residing on the group V sublattice are found to decrease as the input V/III ratio is increased, provided that the partial pressure of the dopant precursor remains constant. The trends are quantitatively explained in terms of the near-thermodynamic-equilibrium condition established at the inter-

Figure 7.13. Growth rate measured using GIXS during growth using TMGa and TBAs as a function of reactor pressure. All flows were constant, and only the total pressure was changed. The V/III ratios ($R_{V/III}$) are 40 (●) and 320 (○) for the data presented. (After Kisker and Kuech [10].)
face. The opposite dependence is observed for volatile dopants on the group III sublattice. The interpretation is dependent on the realization that the V/III ratio at the interface can be altered only by changing the input group V flow rate, as stressed in Section 2.3. Changing the input group III molar flow rate changes the growth rate, not the V/III ratio at the interface.

Even more insight into the application of the consolidated growth model to dopant incorporation can be obtained by considering the only inherent residual dopant for OMVPE growth, namely carbon. We will consider only the most thoroughly investigated systems, the incorporation of C in GaAs grown using either TMGa or TEGa and AsH$_3$. Careful studies of carbon contamination were presented in a series of papers by Kuech and coworkers [64, 67, 68]. They studied C incorporation systematically and thoroughly using the "black-box" approach; that is, they determined the effects of Ga source (TMGa or TEGa), substrate temperature, V/III ratio, and substrate orientation. Carbon contamination is frequently a problem using TMGa as the source and virtually never when TEGa is used. This is simply due to the pyrolysis routes. TMGa pyrolyzes by producing CH$_3$ radicals, whereas TEGa pyrolyzes homogeneously, producing ethene molecules by a $\beta$-elimination reaction, as discussed in Chapter 5.

The dependence of carbon incorporation on orientation, described in Section 3.5.1, is a key piece of evidence demonstrating that CH$_3$ radicals are the culprits. This is significant because it confirms that at least the final stage of TMGa pyrolysis occurs on the surface. Kuech and Veuhoff [67] determined that orientations with larger densities of As surface sites exhibited increased carbon incorporation when TMGa was used as the group III source molecule, as seen in Figure 7.14.

![Figure 7.14](https://example.com/figure7_14.png)

Figure 7.14. Ratio of integrated intensities of carbon peak (1.489 eV) to band-edge luminescence as a function of AsH$_3$/TMGa ratio for various substrate orientations. The GaAs layers were grown at a temperature of 650°C. (After Kuech and Veuhoff [67], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
This was generally supported by the very systematic study of Kondo et al. [69], which showed a dramatic drop in carbon incorporation for misorientation from (001) in either the A or B direction. Others have found dissimilar dependencies on orientation [70, 71]. However, it is generally agreed that methyl radicals are removed from the surface mainly by atomic H and AsH₃ radicals produced from pyrolysis of the AsH₃ or other group V source with at least one H bonded to the group V atom. The increasing pyrolysis rate induced by the surface steps created by misorienting the substrate yields higher surface H (and/or AsH₃ concentrations). The importance of CH₃ is supported by the extremely large carbon concentrations observed using elemental As or AsR₃ (where R is methyl or ethyl), as described in Chapter 4. Similarly, the use of TBAs, which pyrolyzes more easily than AsH₃, thus producing more H atoms as well as AsH radicals, apparently leads to less carbon incorporation when approximately the same temperatures and V/III ratios are used [72], as discussed in Section 4.4.1.7. Additional supporting evidence that the removal of CH₃ radicals occurs only when atomic H from pyrolysis of the group V source is available is the independence of carbon incorporation on the ambient. Substituting He for the normal H₂ ambient has no effect; thus, the H does not come from the ambient. Incidentally, the intentional introduction of methane does not increase the carbon concentration in the solid [68].

It is generally agreed that reducing the growth temperature reduces carbon contamination in GaAs grown using TMGa [73, 74], as will be discussed in Section 8.1.1. For example, the experimental values of both the donor and acceptor concentrations determined by Nakanisi et al. [73] are plotted versus temperature in Figure 8.1. The decrease in donor concentration is due to the decreased pyrolysis of the SiR₄ species commonly present as impurities in TMGa. The reduced carbon concentration has never been thoroughly explained. Several factors acting in opposite directions confuse the picture. As the temperature is lowered, the pyrolysis of TMGa and especially AsH₃ is retarded. Superficially, the former would seem to favor lower carbon incorporation. However, less AsH₃ pyrolysis would increase C incorporation by providing less atomic H on the surface for the formation of volatile CH₄ and by decreasing the As/Ga ratio at the surface, thus increasing the As vacancy concentration that would lead to higher CAS, the C acceptor species observed in photoluminescence and electrical properties measurements. The detailed chemistry studies of Larsen et al. [18] show that at low temperatures the pyrolysis process becomes heterogeneous and, significantly, highly concerted (i.e., the pyrolysis occurs via TMGa-AsH₃ interactions). This reaction produces only CH₄ molecules without production of CH₃ radicals. This provides an appealing interpretation of the increased carbon incorporation at high temperatures: as the temperature is increased, TMGa pyrolysis begins to proceed independently, producing CH₃ radicals in the vapor and on the surface that lead to carbon incorporation into the solid.

An alternate explanation for decreased carbon at lower temperatures may be that the CH₃ radicals are stable enough at low temperatures to preclude the for-
mation of CH₂, CH, and eventually atomic carbon at a surface step, thus hindering C incorporation. No evidence is available to evaluate this hypothesis.

The effect of V/III ratio on carbon incorporation is consistent with the model that CH₃ adsorbed on the surface leads to carbon incorporation. An example of typical experimental data is presented in Figure 7.14 [67]. As the input ratio of AsH₃ to TMGa is increased, carbon incorporation is reduced. The model indicates that this occurs for two reasons: the As vacancy concentration is reduced, and the number of atomic hydrogens available on the surface to remove the CH₃ radicals is increased. Using TEGa, the V/III ratio has no effect on the (always low) carbon concentration in the solid. This is attributed to the less reactive nature of ethyl radicals as well as the β-elimination pyrolysis reaction that produces relatively inert C₂H₄ molecules and leaves a H atom bonded to the Ga.

Finally, the effect of total pressure in the reactor on carbon contamination is easily explained using the growth model discussed earlier. Using TMGa and AsH₃, carbon incorporation is increased as the reactor pressure is lowered [38, 74]. Three factors contribute to this effect: (1) for a given input group V molar flow rate, the partial pressure at the interface is reduced as the pressure is lowered; (2) the surface concentration of AsH₃ is decreased, since it is proportional to the partial pressure at low surface coverage (Eq. [3.1]); and (3) less TMGa-AsH₃ interaction is allowed, leading to more adsorbed CH₃ radicals. This mechanism leads to increased carbon incorporation, because of the increased CH₃ and As vacancy concentrations and the decreased H concentration on the surface. In the extreme case of OMMBE, as mentioned in the last section, the carbon concentration may exceed 10²⁰ cm⁻³.

The effect of reactor pressure on carbon incorporation for GaAs grown using TEGa and AsH₃ was reported by Kuech and Veuhoff [67] to be opposite that observed using TMGa. Reducing the pressure in the range above 76 Torr increased the overall purity. This is probably due to background dopants other than carbon. As the partial pressures of the dopant species are reduced due to the decreased system pressure, the surface coverages are reduced, leading to reduced dopant incorporation. At lower pressures, below 1 Torr, the carbon contamination, even using TEGa, increases [13, 35]. Putz et al. [38] attribute the doping completely to the TEGa. The mechanism is clarified by the results of Horiguchi et al. [36] discussed in Section 7.2.3. The heterogeneous radical elimination reaction for TEGa dominates at low pressures. At higher pressures, where more gas-phase collisions occur, the β-elimination reactions occurring in the gas phase dominate. This inhibits carbon incorporation.

7.4 High-Temperature Regime

The high-temperature regime is considerably less important for OMVPE growth in general. However, it may be important for the growth of Al-containing alloys.
For these materials, a reduction in oxygen contamination is obtained by growth at high temperatures where the Al suboxide is volatile. High-temperature growth has been found to be important for obtaining the best-quality AlGaAs \cite{75}. The use of high temperatures is also important for the III/V nitrides, as discussed in Chapter 8.

As seen in Figures 1.1, 7.1, and 7.3, the growth rate drops with increasing temperature above approximately 750°C. The most convincing arguments and evidence indicate this to be due to depletion of reactants from the gas stream. van de Ven et al. \cite{76} showed that in horizontal systems, heating of the top reactor wall leads to depletion of TMGa due to pyrolysis at the wall. This agrees with the assessment of Heinecke et al. \cite{6}, who also noted much less of a decrease at reduced reactor pressure, as seen in Figure 7.4.

Field and Ghandhi \cite{77} interpreted the drop-off in growth rate at high temperatures and high reactor pressures to a different sort of depletion reaction, namely a homogeneous reaction between partially decomposed TMGa and an As species in the hot zone just above the susceptor surface. Takahashi et al. \cite{78} found that the temperature at which gas-phase depletion becomes important increases with increased flow velocity. They considered the depletion reaction to be homogeneous nucleation of [GaAs]$_n$ clusters in the gas phase caused by the homogeneous pyrolysis of TMGa and AsH$_3$. This would be expected to produce an enormous supersaturation, similar to the situation for the growth of II/VI compounds, which will be discussed in the next section, where homogeneous nucleation is a severe problem. This mechanism is consistent with the observation that lower reactor pressures suppress this depletion. The gas-phase reactions simply have insufficient time to occur before the species reach the substrate surface—that is, as we have observed previously, reduced pressure favors heterogeneous processes.

### 7.5 OMVPE Growth of II/VI Compounds

This detailed discussion gives a good feeling for the kinetic, mass-transport, and thermodynamic factors involved in the OMVPE growth of GaAs over the entire range of temperatures and pressures likely to be encountered. There is little point in discussing other III/V systems since few, if any, new insights into the growth process can be obtained in this way. On the other hand, a description of the OMVPE growth of II/VI semiconductors, which would superficially appear to be similar, reveals new problems and gives new insights into the overall growth process.

The high-band-gap II/VI semiconductors have, for decades, offered the promise of visible emitting devices in the blue region of the spectrum due to their high band-gap energies and efficient luminescence when excited by high-energy electrons or photons. The major problem for growth using normal growth techniques
such as elemental vapor transport, using temperatures of 600° to 900°C, has always been the inability to control conductivity. Some II/VI semiconductors (e.g., ZnS and ZnSe) always tend to be n-type and others (e.g., ZnTe) p-type. This has severely retarded the development of these materials. The difficulty in controlling the conductivity stems from the ease of forming defects in the materials that compensate the added dopants. Movement of the Fermi level by the large distances required to form p-n junctions in these large band-gap materials triggers automatic self-compensation mechanisms associated with the ease of forming native defect levels. Compensation by the H used in OMVPE growth may also play a role in some cases, as discussed in Chapter 8.

The use of low-temperature techniques such as MBE and OMVPE offers a potential solution to this problem, since it should minimize the production of native point defects. A major breakthrough was achieved in 1991 by Haase and coworkers, who demonstrated the growth of highly p-type ZnSe, a material that prefers to be n-type [79]. The key ingredients of the breakthrough were: (1) the very low temperatures in MBE growth, which inhibits the ability of the lattice to form compensating defects, and (2) the development of a plasma source for the low-temperature production of atomic N, a relatively shallow acceptor, in the MBE chamber. The absence of H from the growth process may also facilitate p-type doping by inhibiting one of the compensation mechanisms. This has led to a renaissance in efforts to grow the high-band-gap II/VI semiconductors by OMVPE, which is considered a more suitable technique for production, as discussed in Chapter 1. The currently most promising material appears to be ZnMgSSe. The first short-wavelength (473.3 nm or 2.618 eV) injection lasers produced by OMVPE by Toda et al. [80] used a ZnSe/ZnMgSSe structure grown lattice-matched to the GaAs substrate. The much later growth of successful laser structures by OMVPE is indicative of the difficulties encountered because of the higher growth temperatures, as compared with MBE, due to the need to pyrolyze the precursors and the presence of atomic H, which often acts to passivate dopants.

The poor reliability of these short-wavelength light-emitting devices in II/VI materials grown by any technique is a significant problem. The rapid degradation of laser devices and LEDs may ultimately be due to problems inherent in the II/VI semiconductors—namely, the ease of formation of point defects when the atoms are excited by the large energies (because of the large band-gaps) released in nonradiative recombination events. The recent success of the III/V nitrides, discussed in more detail in Chapters 8–10, makes the ultimate success of these materials for commercial applications in light-emitting devices even less likely.

The other major application for the II/VI semiconductors is infrared detectors operating in the atmospheric window from 8 to 12 µm. HgCdTe alloys can have band-gap energies much lower than those obtainable from common III/V alloys. Traditionally, these materials have been grown by LPE. However, recent developments make OMVPE growth extremely promising.
A major problem for the growth of II/VI compounds is the instability of the commonly available cation organometallic molecules that are liquids at room temperature. The highly volatile group VI hydrides, supplied in high-pressure cylinders, are even less stable: they are known to decompose at room temperature in the cylinder during storage. Thus, the problems with premature reactions encountered in the OMVPE growth of III/V compounds are even more severe for the II/VI semiconductors. They begin at temperatures slightly above room temperature. In fact, the commonly available dimethyl–group II organometallic sources react with the group VI hydrides even at room temperature. These parasitic reactions lead to poor utilization efficiencies of the precursors, poor morphologies, and difficulties with the control of solid composition as well as severe inhomogeneities across the surface of the wafer [81]. These problems plus the hazard associated with the use of the hydrides have resulted in efforts to replace them with liquid, alkyl precursors.

One strategy to minimize the depletion reactions encountered with conventional precursors is the use of low reactor pressures to minimize the number of gas-phase collisions, the same strategy discussed earlier for GaAs growth. Fujita et al. [82] have successfully grown ZnSe using DEZn and H₂Se at 250°C and a reactor pressure of 0.1 Torr. They also used the same technique for the growth of ZnSSe alloys. The growth rate was observed to fall by a factor of 3 from 7.5 to 2.5 μm/h as the pressure was reduced from 10 to 0.1 Torr. This apparently led to improved crystallinity since the band edge to deep-level (self-activated) luminescence ratio increased dramatically as the pressure was reduced. Yoshikawa and coworkers [83, 84] grew both ZnS and ZnSe using a similar approach.

Another approach has been to develop more stable source molecules such as the common dialkyl-selenides and -sulfides DMSe and DMS. This reduces the hazard associated with the use of the hydrides. However, the higher bond strengths require high growth temperatures of 450°C and higher. Similar high growth temperatures are also required for theoretically less stable precursors such as DESe and DASe [85]. These temperatures would be no problem for the III/V semiconductors. However, the perennial problem with II/VI compounds due to non-stoichiometry, discussed earlier, prevents the achievement of high conductivity levels. An additional problem is that the most desirable p-type dopant, nitrogen, is not efficiently incorporated into the lattice at high growth temperatures. The use of low growth temperatures is considered absolutely essential for the successful growth of p-type ZnSe, ZnSSe, and related alloys.

The use of both Zn and Se alkyls to eliminate the premature reaction problems [86] allows an investigation of the growth process without interference from the parasitic reactions, which we are not particularly interested in understanding: their total elimination is the goal. The study of Mitsuhashi et al. [86] is worth considering in some detail, since it gives insight into the similarities and differences between the OMVPE growth processes for II/VI and III/V semiconductors.
7.5 OMVPE Growth of II/VI Compounds

The epitaxial layers of ZnSe were grown on GaAs substrates at a total reactor pressure of 300 Torr. As seen in Figure 7.15, the behavior of growth rate versus temperature is similar to that observed for GaAs. The growth process is controlled by surface reaction kinetics at temperatures below approximately 500°C, and the growth rate is independent of temperature at higher temperatures, indicating that the growth process is controlled by mass transport. The choice of alkyls has a small but consistent effect on the growth rate. The slowest growth rates are obtained using DESe combined with either DMZn, shown in Figure 7.15, or DEZn.

In the mass-transport regime, the molar flow rates of both the group II and group VI sources affect the growth rate, as seen in Figures 7.16 and 7.17. The behavior appears dissimilar to that for III/V systems. Since both reactants are quite volatile, the II/VI ratio can be easily made either larger or smaller than unity. When the DESe flow rate exceeds that of DEZn in Figure 7.17, the growth rate becomes a sublinear function of DESe flow rate and eventually saturates. Similarly, when the DEZn flow rate is much smaller than the DESe flow rate, the dependence is linear. However, the growth rate appears to saturate with increasing DEZn flow when it exceeds that of DESe. This behavior is qualitatively consistent with the model that the minority element is depleted at the interface because of the high supersaturation in the input vapor. The model predicts that when component A has a much higher partial pressure than component B, the growth rate will be a linear function of $p_B$ and independent of $p_A$. When the two partial pressures are comparable, the growth rate will increase sublinearly with both partial pressures.

At a lower temperature of 440°C, where the growth process is thermally activated, the growth rate is a function of the DESe flow rate but is independent of
DEZn flow rate. This indicates that the surface kinetic step limiting the growth rate is related to the Se source. Interestingly, the activation energy is nearly independent of the choice of source molecules, being in the range of 22–24 kcal/mol for all combinations. Therefore, the kinetic process must not be simply the pyrolysis of the group VI alkyl. Mitsuhasi et al. [86] proposed that the growth proceeds by a sequence of steps. In the low-temperature region of the reactor, the Zn precursor molecule decomposes to give metallic Zn. At higher temperatures, the Se alkyl reacts with the ambient, forming H₂Se. The reactants on the surface involve

Figure 7.16. ZnSe growth rate versus DEZn molar flow rate for growth at 520°C. The open and filled circles indicate the growth rate for a DESe flow rate of 20 \( \mu \text{mol/min} \) and the open squares for a DESe flow rate of 60 \( \mu \text{mol/min} \). (After Mitsuhashi [86], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)

Figure 7.17. ZnSe growth rate versus DESe molar flow rate at 520°C and a DEZn transport rate of 10 \( \mu \text{mol/min} \). (After Mitsuhashi et al. [86], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
Zn and H$_2$Se. The activation energy for this heterogeneous reaction to form ZnSe and H$_2$ is the rate-limiting step for the growth process. Thus, it is independent of the alkyl sources. The differences in growth rate for the various sources was ascribed to a limited amount of parasitic reactions.

Design of novel S and Se precursors using a strategy similar to that used for the group V hydrides appears to be required. The use of diisopropylselenide (DIPSe) allows a slight reduction of growth temperature. However, the use of tertiarybutyl ligands is much more effective. Growth using ditertiarybutyl-Se and -S was found to eliminate parasitic reaction problems and to allow the growth of ZnSSe alloys at temperatures as low as 330°C [87, 88].

Other alternate precursors are methylallyl selenide (MASe) and diallyl selenide (DASE) [81]. They allow OMVPE growth at temperatures of approximately 400°C but give extensive carbon contamination levels of $10^{20} - 10^{21}$ cm$^{-3}$. Carbon is not electrically or optically active in ZnSe, but at these levels can compromise the crystalline quality of the epitaxial layers. Tertiarybutylallylselenide (TBASe) allows growth at temperatures as low as 350°C without carbon contamination. As seen in Figure 7.18, for a VI/II ratio of 2, pyrolysis of the Se precursor limits the ZnSe growth rate in the low-temperature, kinetically limited regime.

Alternative potential S precursors include thiophene (C$_4$H$_4$S) [89], tetrathio- phene (C$_4$H$_8$S) [89], and methylmercaptan (MSH) [90], discussed in Chapter 4. CS$_2$ reacts with the H$_2$ ambient forming the hydride, but only at temperatures high enough to avoid low-temperature prereaction problems [91].

The common precursors used for the growth of Mg-containing II/VI alloys and for the doping of III/V semiconductors are cyclopentadienyrmagnesium (Cp)$_2$Mg and bismethylcyclopentadienyl-magnesium (MeCp)$_2$Mg. The former is a solid at room temperature and the latter a liquid.

![Figure 7.18](http://example.com/figure7.18.png)  
**Figure 7.18.** Growth rate of ZnSe as a function of temperature for several alkyl selenide sources. MASe (■), DASE (●), and TBASe (○). (After Danek et al. [81], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
Another approach to avoiding the parasitic reaction problems plaguing the early OMVPE growth of II/VI semiconductors is to design cation precursors that will not engage in adduct forming reactions. This is most easily accomplished by beginning with sources that are already adducts, such as DMZn-TEAm. In addition to the inhibition of parasitic reactions with the group VI sources, the adduct sources have other advantages. They are easier to handle and purify, which, in principle will lead to higher purity layers. They also have much lower vapor pressures. In fact, the vaporization process may involve dissociation of the adduct before vaporization, which may be a disadvantage in terms of minimizing parasitic reactions, since the adduct exists almost entirely in the liquid phase. This has led to the recent terminology *entrained partial pressure* to describe the transport of DMZn from an adduct source. By this measure, the partial pressure of DMZn is 2.5–3.5 Torr at room temperature [92]. However, this leads to a distinct advantage of using these precursors as dopants in the growth of III/V semiconductors, since the high vapor pressures of many group II precursors require complex dilution schemes to reach the low partial pressures desired in the reactor. The dissociation of the adduct brings into question the simple interpretation of the role of the adduct in inhibiting parasitic reactions. A likely explanation, based on the effect of the presence of amines themselves, is that this is entirely a surface effect [93].

An important requirement for the growth of II/VI structures for visible emitting devices is a suitable p-type dopant. As discussed earlier, nitrogen is the leading contender. One possibility is to use plasma sources to dissociate N\textsubscript{2} to produce the required atomic nitrogen. This approach can be used for OMVPE [94], although the results have not been satisfactory to date. The alternative is to use N precursors that pyrolyze efficiently at low temperatures by routes that yield N incorporation into the solid. Heuken et al. used triallylamine (TAN) and bistrimethylsilylamidozinc (ZnBTM). Both give N in the solid for growth at low VI/II ratios. However, the samples remain n-type, even when significant concentrations of N are incorporated into the solid. An early indication of success in the N doping of the high-band-gap II/VI semiconductors was the use of tertiarybutylamine (TBAm) for the growth of ZnSe on GaAs substrates using DEZn and DMSe at a temperature of 350°C and a reactor pressure of 200 Torr. An important part of the growth apparatus was photoirradiation of the sample during growth using a Hg lamp. The measured p-type doping level was 10\textsuperscript{17} cm\textsuperscript{-3} [95]. The first injection lasers made in ZnMgSSe grown by OMVPE using the precursors DMZn, DMCd, DES, (MeCp)\textsubscript{2}Mg, and DMSe used diisopropylamine (DIPNH) as the p-type dopant with UV irradiation from a high-pressure Hg lamp. p-type doping levels of only 10\textsuperscript{16} cm\textsuperscript{-3} were reported, 100× less than the N concentration in the solid [80]. This brief summary of the literature makes it clear that one main reason that OMVPE trails MBE for the growth of II/VI laser diodes is the difficulty in p-type doping using nitrogen.

An example of another difficulty introduced by the high pyrolysis temperatures
of the common group VI alkyls is demonstrated by the extreme difficulty encountered in the OMVPE growth of HgCdTe. DMCd pyrolyzes between 200° and 300°C. The only available Te source until recently was DETe, which pyrolyzes homogeneously at 410°C. This is reduced to 350°C in the presence of a Te surface. The presence of DMCd is found to lower the DETe pyrolysis temperature by 100°C, similar to the effect of TMGa on AsH₃ pyrolysis, described in Chapter 5. The effect was first attributed to a vapor-phase adduct [96]. However, Bhat et al. [97] later showed that elemental Cd has the same effect. The Hg source is typically elemental Hg, which has a high vapor pressure, rather than the Hg alkyls, which are extremely toxic and do not pyrolyze in the atmosphere, as the group III sources do, to yield the much less hazardous oxides. Unfortunately, Hg does not have the favorable effect of lowering the DETe pyrolysis temperature. The net result is that the optimum temperature for CdTe growth is approximately 350°C, while the optimum temperature for HgTe is higher, approximately 410°C. In addition, the larger enthalpy of formation of CdTe (−24.6 kcal/mol) as compared with HgTe (−8.1 kcal/mol) makes the growth of high-Hg alloys difficult.

One approach to the problem is the clever mechanical solution of growing a CdTe/HgTe superlattice [98]. When heated to moderate temperatures, the high solid-state interdiffusion coefficients lead to a homogeneous HgCdTe alloy by IMP (interdiffused multilayer process). This is discussed in detail in Section 8.10.1.2.

Another approach is to use photons to dissociate the molecules at the low temperatures desired for HgCdTe growth. The UV photons absorbed by the OM sources are energetic enough to disintegrate the molecules and release the elements. This leads to unwanted homogeneous nucleation, which induces particulate formation in the vapor leading to nonepitaxial growth. It is essential that the photolysis be achieved on the surface to stimulate only the desirable heterogeneous process. Irvine et al. [99] have produced high-quality HgTe at temperatures as low as 200°C using DETe in H₂ with stimulation by photons from a high-pressure Hg vapor lamp. Details of the growth technique are given in Section 8.10.1.4.

Another interesting solution is the development of new organometallic Te sources, as discussed in Chapter 4. A comparison of the results from these various sources gives additional information about the growth process. Since the HgTe and CdTe growth rates are empirically proportional to the Te source partial pressure, the growth process is perhaps least ambiguously described in terms of the growth rate constant, the growth rate divided by the partial pressure of the Te source. The temperature dependence of the growth rate constants for HgTe using several Te precursors are compared on an Arrhenius plot in Figure 7.19. At a constant reactor pressure, the mass-transport-limited growth rate constant will be roughly the same for all sources, since the diffusion coefficients vary only slightly. A value of slightly over 10⁴ μm/h/atm is suggested by the data for both DTBTe and DIPTe. Two other sources give temperature-independent rate constants over
Figure 7.19. Growth rate constant (growth rate/partial pressure of Te source) versus temperature for the growth of HgTe using several Te precursor molecules. Included are data for DETe [103], DIPTe [103, 186], DTBTe [186], and DNPTe [186] from Hoke and Lemonias. Additional data for DETe are from Bhat and Ghandhi [102]. Data for photon enhanced HgTe growth using DETe are from Irvine et al. [104].

the entire temperature range studied. DHTe gives a temperature-independent growth rate for temperatures of \( \geq 250^\circ C \) [100]. A temperature-independent growth rate was also reported for MATe to temperatures as low as 290°C [101]. At lower temperatures the growth rate was controlled by pyrolysis of the DMHg source.

In the kinetically limited regime, the growth rate constant is seen to be highly dependent on the nature of the Te source molecule. The rate constant clearly increases as the stability of the Te precursor molecule decreases. As discussed in Chapter 4, the Te-C bond strength can be predicted in terms of the number of carbon atoms bonded to the carbon participating in the Te-C bond, \( n^0 \). DMTe, with no carbons bonded to \( C_{Te} \), is too stable to be a useful OMVPE source. Considering only the practical sources included in Figures 4.7 and 7.19, the lowest growth rate constants are for DETe, where \( n^0 = 1 \). Similar growth rate constants
are determined using DNPTe. The \( n \)-propyl radical also has a value of \( n^0 = 1 \). The growth rate constant for DIPTe, where \( n^0 = 2 \), is larger by an order of magnitude. The rate constant increases by more than another order of magnitude when \( n^0 = 3 \), as demonstrated by the data for DTBTe. A comparison of the Arrhenius plots in Figure 7.19 in terms of the \( A \) factor and the activation energy, \( E^* \), is also revealing. The major effect of changing the C-Te bond strength is to change the activation energy for growth. Using DETe, the activation energy from the data of Bhat and Ghandhi [102] is approximately 30 kcal/mol, as shown by the line through the data points. The value of \( E^* \) for the DIPTe data of Hoke and Lemonias [103] is also approximately 30 kcal/mol. For HgTe growth using DTBTe, the activation energy is lower, with a value of 24 kcal/mol for the line drawn through the data points in Figure 7.19. The \( A \) parameter appears to be approximately \( 10^{13} \) 1/mol-s, independent of the nature of the Te source molecule. The data indicate that the homogeneous pyrolysis rate of the Te precursor molecule determines the growth rate of HgTe in the kinetically limited regime. The only precursor for which independent pyrolysis data was available is DETe. An approximate value of 25 kcal/mol was reported from the pyrolysis study by Irvine et al. [104].

The effect of changing the Te precursor for HgTe growth is similar to the effect of changing the Ga precursor for GaAs growth, as shown in Figure 7.3. In that case the main effect also appears to be the change in the activation energy for growth.

An interesting addition to the comparison of growth rates in Figure 7.19 is the data obtained for DETe with the use of photons by Irvine et al. [105] discussed earlier. Photostimulation allows the grow of HgTe at temperatures in the range from 180° to 250°C where unassisted growth using DETe is impossible. Extrapolation of the HgTe growth rate using the DETe source in the dark to lower temperatures indicates the effect of the photons to be large, increasing the growth rate by approximately three orders of magnitude. The activation energy was reduced from 30 to 24 kcal/mol by the photons, as indicated by the line through the data points. The effect of photon irradiation appears to be largely due to a reduction in the activation energy for pyrolysis of the DETe.

The OMVPE process appears to be yielding results approaching the results obtained for the more well-established LPE technique. For example, Mitra et al. [106] have grown high quality HgCdTe using the IMP process at a temperature of 360°C on CdZnTe substrates. The sources were DMCd, DIPTe, and elemental Hg. The most common donor element is In. However, In precursors, including TIPIn, prereact with Te alkyls, giving adducts that deplete the nutrients from the reactor. Iodine is apparently a better donor, using ethyliodine (EI) as the precursor. It has no memory and is 100% activated, giving controlled doping in the range of \( 10^{14} \) to \( 10^{18} \) cm\(^{-3}\). It also has a low diffusivity in HgCdTe and yields materials with better mobilities and longer lifetimes than obtained for In. The I incorporation
efficiency was found by Mitra et al. to have a pronounced orientation effect for nominally (001) substrates, with $I$ values ranging from $10^{15}$ atoms/cm$^3$ for a mis-orientation of $8^\circ$ to $10^{18}$ cm$^{-3}$ for the (211) orientation.

Arsenic is typically used for p-type doping, with success obtained using TBAs [107] and phenylarsine [108]. However, Mitra et al. report superior results using TDMAAs. The lower vapor pressure, listed in Table 4.7, which is a handicap for the OMVPE growth of the III/V arsenides, is beneficial for a dopant in HgCdTe. However, all of the organometallic As precursors prereact with the Cd precursor, forming adducts. These parasitic reactions result in a variation in alloy composition.

7.6 Design of the Overall Process

From time to time during our development of the overall model for the OMVPE process, we have discussed the selection of individual growth parameters, such as V/III ratio, temperature, total pressure, and so forth. At this point it is worthwhile to consider the process as a whole and discuss each of the major decisions involved in designing both the reactor and the growth process. Naturally, this sort of selection process depends on the ultimate application. The parameters may be different for a large-scale production process for GaAs solar cells than for a small-scale process for the production of quantum-well lasers. Nevertheless, we can summarize the application of our fundamental understanding to the design process.

7.6.1 Reactor Geometry

The first decision relates to the overall geometry. Giling and coworkers [109, 110] were the first to remind the OMVPE community forcefully of the importance of simple guidelines for the design of hydrodynamically appropriate reactors. As discussed in Chapter 6, they suggested that the presence of sudden changes in the diameter of the reactor, the presence of obstacles, and recirculating convection currents due to heating of the gases could limit the ability of reactors to provide uniform growth rates and abrupt changes in solid composition. Figure 7.20 illustrates schematically several of the problems in each category routinely found in early OMVPE reactors. Hydrodynamically correct solutions are also suggested. For example, to avoid the eddy currents indicated in Figure 7.20a for a change in the size of the reactor, the angles used must be less than $7^\circ$ to avoid eddy currents. Vanes can be used to avoid these recirculating currents when the angles must be greater than $7^\circ$. A more elaborate solution is the use of complex, nonlinear shapes for the expansion region to avoid eddy currents [111, 112], as illustrated in Figure 7.21. An additional practical consideration for reactor design is obviously the
7.6 Design of the Overall Process

avoidance of unpurged “dead” volumes, an example of which is indicated in Figure 7.20c. Some reactors use specially machined low-dead-volume four-way valves. For abrupt changes in composition, a facility for rapid switching of the input gases from vent to run lines at a position very near the input to the reactor tube is required. Care must also be exercised to avoid pressure differences between vent and run lines that are known to produce undesirable transients in the gas-phase composition. This can be accomplished by appropriately designing the lines to present approximately the same pressures for the vent and run lines at the three-way valves, or by installing baratrons that automatically adjust the flow through the vent line to reduce the pressure difference between vent and run lines to very small values [113]. Finally, complete mixing of the gases where the cation and anion precursors arrive at the reactor from separate lines must also be ensured [112, 114].

The earliest OMVPE studies used vertical reactors with the gas flow directed downward of the type shown in Figure 6.4. These are capable of producing outstanding results, but based on our understanding of gas flow, such configurations

Figure 7.20. Examples of improper reactor design. (a) Return flow patterns due to a sharp increase in tube diameter. (b) Return flow patterns due to thermal expansion and contraction of the gas. (d) Unpurged spaces that act as virtual leaks. (After Giling and van de Ven [110].)
are very likely to produce recirculating regions, as discussed in Chapter 6, which enhance premature reactions and make the rapid change of gas phase composition impossible. As a result of the recirculating currents, the growth rate and alloy composition will typically vary widely across the surface of the susceptor. A very common solution is to rotate the susceptor during growth. This simply averages the effects to make the wafer symmetrical about the axis of rotation. The result is a significant increase in uniformity. A more sophisticated and elaborate solution, discussed in Chapter 6, is to spin the susceptor rapidly to sweep the gas across the substrates [115, 116]. With the proper injection scheme, this produces a uniform mass-transport rate to the susceptor and so leads to increased uniformity. This type of reactor, seen in Figure 7.22, is available commercially from EMCORE with a capacity of 38 2" wafers. Reactors of this size are required for the large-scale production of devices such as solar cells and high-brightness light-emitting diodes [115, 116, 117].

Another approach to avoiding recirculating currents in a nominally vertical reactor is to keep the distance between the susceptor and the top wall small, as in the radial flow reactor described by Frijlink et al., seen in Figure 7.23, which ends up being a horizontal, radial-flow geometry [118]. The rapid gas velocities produced in this reactor minimize parasitic reactions and result in very efficient use of precursors. This type of reactor is also available commercially from Aixtron. The platen of the AIX 3000, with five rotating 10" substrate holders, is shown in Figure 7.24. Ninety-five 2" wafers, with an area of nearly 2,000 cm², can be handled in a single run.

Figure 7.22. Photograph of EMCORE reactor system. (Courtesy of EMCORE Corp.)
Both types of large-scale commercial reactors described here are capable of producing thickness, alloy composition, and doping uniformities of approximately ±1% over large areas by selection of optimum growth parameters [115,
Even better control can be demonstrated when *in situ* controls are instituted, as discussed in the next section. Issues of uniformity are addressed in more detail in Section 8.1.7.

Alternatively, natural convective forces can be used beneficially by inverting the reactor, as shown in Figures 6.4 and 6.5, with the reactants entering at the bottom, flowing past the substrate, which is mounted upside down, and exiting at the top [120]. The "chimney" reactor, shown in Figure 7.25, represents an apparently similar approach with the substrates mounted on the sides of the reactor tube [121]. This results in atomically abrupt GaAs/AlGaAs interfaces. In this reactor Leys et al. have made a subtle change to an essentially horizontal reactor, since the gas flow is nearly parallel to the substrate surface. With the gases entering at the top, the reactor becomes the conventional barrel reactor, which is a popular type for large scale processes where 20–30 wafers are processed per run. Gersten et al. [122] have reported the use of such reactors for the growth of solar cell materials with 1,080 cm² of material processed per run in a three-tiered barrel reactor. The GaAs thickness uniformity was reported at that time to be as good as ±10% over most of the area with comparable doping uniformities along the direction of gas flow. The composition of AlGaAs alloys was reported to be within ±3% over the entire surface. Hayafuji et al. [123] reported even better uniformi-

Figure 7.25. Schematic diagram of chimney-type reactor. The gas inlet is at the bottom of the reactor tube, and the substrates are mounted on the inside of the hollow, pipe-shaped susceptor with a rectangular cross-section. (After Leys et al. [121], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
ties in a similar commercial barrel reactor operating at 130 Torr. In the Cambridge Instruments MR-200, 20 substrates 2" in diameter can be processed simultaneously. The thickness uniformity over the 20 wafers was reported to be ≤8%. The variation in Al content was ≤1% along the gas flow direction and among 10 2" wafers. Similar reactors with six 3” wafers per run have been reported to yield uniformities of 2% [124].

The other reactor geometry used in early reactors uses horizontal gas flow, nearly parallel to the wafer surface. This is the simplest reactor geometry capable of producing good uniformity along with abrupt changes in solid composition. With the proper aspect ratio and a high flow velocity, return flows at the heated susceptor are avoided, as discussed in Chapter 6. Cooling of the top surface is sometimes used to prevent excess depletion of the nutrients from the gas stream. Smoothly decreasing the channel opening can be used to compensate for depletion of the alkyls from the gas, yielding both uniform growth rate and solid composition without resorting to substrate rotation. This may be accomplished using a tapered cell, a tilted susceptor, or a tilted baffle mounted above the susceptor. This is the reactor design commonly used for single-wafer research reactors.

Properly designed atmospheric-pressure horizontal reactors are capable of producing a high degree of uniformity over substrate areas of a few square inches (10s of square centimeters). For larger areas, two approaches are the use of rotating substrates and/or lower reactor pressures. Tanaka et al. [125] demonstrated thickness uniformities of approximately 1% over three 2" diameter substrates through the use of rotation in a horizontal reactor. More recently Arai et al. [126] demonstrated the growth of either six 3" or 18 2" wafers in a horizontal reactor operated at a total pressure of 50 Torr. The substrates are mounted upside down to avoid gas recirculation and rotated at 20 rpm. The reactor is shown schematically in Figure 7.26. The uniformities of thickness and doping for GaAs layers were both ±2%.

![Schematic diagram of a novel OMVPE reactor.](image-url)
7.6.2 In Situ Controls

As indicated in Chapter 1, a distinct advantage of MBE versus OMVPE during the early neck-and-neck race for the development of these techniques for advanced devices during the 1970s and 1980s was the ability to monitor the condition of the surface using RHEED. Using this technique, the desorption of the oxide to form the reconstructed semiconductor surface could be monitored. The effects of growth parameters on the surface structure, the roughness, and the growth rate could be observed in situ during the growth run. This led to the rapid optimization of growth processes for various materials and device structures. For OMVPE, on the other hand, the electron beam is attenuated by the atmosphere, so the optimization process has been much slower because the material grown in a run could only be analyzed ex situ. In addition, once the optimization was complete, efforts to maintain the process concentrated on keeping flow rates and temperatures constant. Since these always vary with time, especially when routine changes are made, a great deal of effort was wasted on test runs, the growth of nonoptimized materials, and repeated reoptimization of the process. A simple example of the value of real time monitoring of the OMVPE process is the use of an in situ technique to detect exhaustion of a source bubbler or the failure of a flow controller. Immediate detection allows the run to be aborted at an early stage. This results in a tremendous savings in time and materials, especially for production operations where the same structure is produced repeatedly. In addition, inevitable changes in the growth process lead to nonuniform layers and run-to-run nonreproducibility. For a production process, such problems reduce yield and are thus extremely expensive.

The desire for the maximum usage of reactor time and materials and a high yield for very complex structures virtually requires that the process be monitored in situ during the growth process. Fortunately, a number of techniques for in situ monitoring of the OMVPE growth process have been developed in recent years. They will be described briefly in this section. The ultimate goal is, of course, to monitor all of the important features of the materials and structures being grown and to use these measurements as feedback to control the process. The current reality falls short of this goal. However, in situ monitoring can be used as feedback on layer thickness and material composition for use in control of the process. Very often, a “fingerprint” of the optimum structure can be generated using the optical techniques described. Deviations from this signature can be used as the basis for termination of the growth and to pinpoint the likely causes. These developments have led directly to improved uniformity and reproducibility and to the elimination of many wasted runs and test runs.

Because RHEED cannot be used to monitor the OMVPE process, the development of in situ monitoring tools has concentrated on other techniques. For fundamental studies, grazing incidence X-ray scattering has been used in place of RHEED for OMVPE reactors. However, most practical growth monitoring has
concentrated on optical techniques. The photons generated by the sample itself produce oscillations due to interference effects that have been used for decades to measure the thickness. Today, similar techniques have been refined for the closed-loop control of the growth of complex structures such as the distributed Bragg reflectors used in vertical cavity surface-emitting lasers (VCSELs) [127].

Ellipsometry is a tool long used for the characterization of thin films. It yields the film thickness and the refractive index, which can be used to obtain the composition of a ternary alloy. Early attempts to use this technique for monitoring the OMVPE growth process were only partially successful, because of the complexities of implementing and interpreting the results [128]. More recent studies using normal incidence reflectivity at a single wavelength, from an external laser source, to monitor the growth have proven useful, as will be described later. This technique is relatively simple to implement and is now becoming a common tool for production-scale reactors. In many cases, the detailed interpretation of the results is still missing. However, the signature produced by a particular reconstruction or structure in the solid is nevertheless highly useful in monitoring the growth process.

A real breakthrough in optical characterization of the surface during growth came with the pioneering work of Aspnes and coworkers [4, 20, 21, 22], who showed that the surface reconstruction could be inferred from the electronic states on the surface determined using reflectance spectroscopy, in particular the anisotropy of the surface that is not seen in the bulk. Since electronic transitions are monitored, it is impossible to determine directly the surface reconstruction, which relates to the long-range periodicity of the surface. However, over the years a reliable one-to-one correlation has been established between particular RDS spectra and certain surface reconstructions, as discussed in Chapter 3. Also discussed is surface photo absorption (SPA), a similar technique using the Brewster angle to minimize bulk contributions to the signal, which has been shown to yield similar information. p-polarized reflectance spectroscopy (PRS) is a related technique preferred by some groups [129].

Since a wide range of optical techniques is now used for the monitoring of the OMVPE process, this entire subsection will be devoted to a discussion of the individual techniques. The \textit{ex situ} and \textit{in situ} characterization of the gas-phase composition are discussed first, followed by a discussion of the techniques for \textit{in situ} characterization of the surface and the compositional profile of the epitaxial layers being grown.

\subsection{Ex Situ Characterization of Gas-Phase Composition}

Traditionally, control of the solid composition of semiconductor epitaxial layers grown by OMVPE has relied on control of the flow rates of the carrier gases and
the temperatures of the source bubblers. This is generally acceptable for well-filled bubblers when the source is a liquid. However, when the source is depleted, the gas may not be completely saturated, leading to a reduction in the reactant partial pressure. Even more problematic is the use of solid sources, such as TMIn. As the surface area of the source granules increases during storage or use the vaporization rate may decrease, resulting in a nonsaturated vapor exiting the "bubbler," as seen in Figure 7.27. This also results in a constantly decreasing TMIn supply with bubbler usage, as shown in Figure 7.28. The common approach of simply adjusting the flow rate to compensate is not very effective. It results in the waste of many growth runs because the solid produced does not have the desired composition. Of course, the material produced is also nonuniform. A very effective solution to this problem is to measure the actual concentration of the

Figure 7.27. Vapor pressure of a TMIn source versus run number. The hydrogen flow was 34 sccm. (After Stagg et al. [130], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)

Figure 7.28. Variation of TMIn concentration with hydrogen flow rate. (After Stagg et al. [130], reprinted from the Journal of Crystal Growth with permission from Elsevier Science.)
precursor in the vapor during growth and to use this quantity to control the flow rate of the carrier gas. The first technique used to measure the precursor concentration relies on the variation of acoustic velocity with vapor composition [130]. The EPISON is a commercial product (manufactured by Thomas Swan and Co. Ltd., Cambridge, England) that has been found to be a highly reliable and useful part of modern OMVPE reactors [131].

Fourier transform infrared (FTIR) spectroscopy has also been used for the ex situ measurement of the composition of the vapor stream(s) entering the reactor [132, 133]. The technique relies on the use of newly developed fluoride and chalcogenide infrared fibers to measure the C-H vibrational stretching modes that absorb in the 2,800-3,000 cm\(^{-1}\) range and the rocking and bending modes in the 1,900-1,000 cm\(^{-1}\) range. It has the advantage of being capable of monitoring the concentrations of several species in a gas mixture, since each species has a unique absorption spectrum. The results of Sugiyama et al. [133] showed that the molecules exiting a bubbler may not initially be those expected. For example, during the first 20 mins of use, significant quantities of arsine are evolved from a TBAs bubbler. Salim et al. [132] used this technique to monitor simultaneously the concentrations of TMGa, TMIn, TBP, and TDMAP. The reported detectivity limits are somewhat high for accurate control of the typical OMVPE growth process. The acoustic technique works only when the vapor contains the carrier gas and a single precursor, since it sums the effects of each precursor on the acoustic velocity in the vapor.

### 7.6.2.2 In Situ Characterization of Gas-Phase Composition

Ultraviolet (UV) spectroscopy may be used to monitor the vapor composition directly above the susceptor [134]. This is, of course, the most direct parameter for control of the growth rate and the solid composition, including the addition of dopants to the solid. Each precursor has a unique UV absorption signature. This technique can also be used to study the growth chemistry, since it can be used to monitor intermediate species formed during the pyrolysis and growth reactions, as described in Chapter 5 [135]. Of course, FTIR spectroscopy can also be used for in situ determination of vapor-phase composition.

### 7.6.2.3 In Situ Characterization of the Epitaxial Layer

**Laser Scattering**

Perhaps the most obvious technique for monitoring the surface roughness during vapor-phase epitaxial growth is diffuse (nonspecular) optical scattering. The diffuse scattering is nil for a perfectly smooth surface and increases with increasing
surface roughness. In recent developments, this simple technique of laser light scattering (LLS) has been shown to give information about features as small as atomic steps, allowing the evolution of steps to be followed during OMVPE growth. Epler et al. report the use of a 10-mW HeCd laser (442 nm) to irradiate the surface during growth. The intensity of the scattered light at right angles was monitored for a rotating substrate [136]. Surprisingly, they detect intensity oscillations due to the growth of sequential monolayers, similar to the RHEED intensity oscillations used to monitor layer-by-layer growth in a UHV environment. This is an impressive result for such a simple, easily implemented, and robust technique.

LLS has also been used to monitor the formation of elliptical islands during the CBE growth of GaAs as well as the cross-hatch pattern due to lattice-parameter mismatch during growth of GaInAs [137].

**Laser Reflectometry**

Ellipsometry is a well-known technique for the characterization of the refractive index and thickness of thin films [138]. Traditionally, this measurement is performed at multiple wavelengths with the angle of incidence equal to the Brewster angle. Spectrometric ellipsometry can be used kinetically to monitor the OMVPE growth of GaInAsP [151]. It may prove to be extremely useful in optimization of the complex switching process required to produce abrupt GaInAs/InP interfaces, as described in Chapter 9. Much more easily implemented single-wavelength variants are more commonly used to determine the combination of layer thickness and solid composition (from the known composition dependence of refractive index) during growth. This has been used for the in situ control of growth rate, layer thicknesses, and Al content of AlGaAs layers grown by OMVPE. Since the growing layer is transparent to the laser irradiating the sample, this technique is simply tracking interference versus time, which is, of course, determined by the combination of thickness and refractive index. If the growth rate is constant, the oscillation period changes at, for example, a GaAs/AlGaAs interface. In this case, it can be used for the in situ measurement of the Al content of the AlGaAs layer [139, 140].

Single-wavelength laser reflectometry at normal incidence has become an extremely useful tool for OMVPE reactors. The complex pattern (fingerprint) produced during the growth of a multilayered structure can be used to detect abnormalities in the growth process. A pattern is established for a successful growth run, and departures give an indication of problems in the growth process. This is a robust technique that is widely applicable for quality control. Application of sophisticated models allows the reflectance patterns to be interpreted in terms of the real-time growth rate and solid alloy composition [141]. This technique can be used to monitor the growth of extremely complex structures such as VCSELs.
The result has been a significantly improved uniformity and yield [143]. Of course, the technique can also be applied to the monitoring of other systems, such as the II-VI semiconductors [144, 145].

Pyrometric Interferometry

Rather than using light incident from an external source, the filtered infrared photons emitted from the heated sample can also be used to perform interferometric measurements [146] allowing the monitoring of thickness, temperature [147], and composition [148] during growth. This is a versatile, robust tool easily installed on CBE and OMVPE reactors that is suitable for close-loop control of the growth of complex structures, such as GaAs/AlGaAs VCSELs [149]. As an example, Sato et al. [150] demonstrated the use of filtered thermal radiation at 940 nm collected normal to the sample surface to monitor and control the growth of quarter-wavelength-distributed Bragg reflectors in the GaInP/AlInP system grown using GSMBE.

Physical Techniques for Monitoring Surface Reconstruction During Growth

As mentioned, RHEED has been used for many years for the in situ determination of the condition of the surface during growth under UHV conditions. RHEED oscillations can also be used to monitor the growth process one monolayer at a time. An equivalent physical scattering technique, described in Chapter 3, applicable to OMVPE is the use of grazing incidence X-ray scattering (GIXS). Unfortunately, this requires a sophisticated high-intensity, scanned X-ray source such as a synchrotron. Since there are few of these expensive tools, this will never be a widely used characterization technique. However, as discussed in detail in Chapter 5, studies of X-ray scattering have provided important information about the fundamental aspects of the OMVPE growth process [10]. As for RHEED, oscillations corresponding to the growth of individual monolayers are observed. So the growth rate can be accurately monitored in situ during growth.

7.6.2.4 In Situ Characterization of the Surface Structure and Reconstruction

Early attempts to monitor the OMVPE growth process in situ used ellipsometry [128]. Interest in spectrometric ellipsometry has reemerged recently. Sudo et al. [151] used this technique very effectively for the optimization of the GaInAs/InP in quantum-well structures, as described in more detail in Chapter 9.

Nevertheless, other optical tools have received much more attention because of
the need for simplicity. The most important optical techniques for monitoring the state of the surface during OMVPE rely on the breaking of the symmetry of the crystal at the surface due to reconstruction. For example, formation of [110] rows of group V dimers on the \((2 \times n)\)-reconstructed \((001)\) surfaces breaks the symmetry of the [110] and [\(\bar{1}\)10] directions in the zincblende (or diamond cubic) solid. This makes the difference spectroscopies based on the original RDS observations of Aspnes and coworkers \([20–22]\) useful. These techniques are especially useful for OMVPE where the \textit{in situ} probes that use electron beams, such as RHEED, cannot be used. The long-range periodicity of the surface cannot be determined from optical techniques such as RDS and SPA. Since they are based on the use of UV photons, they simply measure electronic transitions related to the surface states. However, a close correlation between certain reconstructions measured using RHEED and unique RDS (or reflectance anisotropy spectroscopy, RAS) and SPA spectra has given a growing confidence that these types of measurements can be used to give a good indication of the surface reconstruction during growth, as discussed in Chapter 3. Similarly good correlations between GIXS and RDS strongly indicate that most surface reconstructions of \((001)\) GaAs can accurately be determined using RDS.

The \((001)\) surface-phase diagrams observed for GaAs layers grown by OMVPE and MBE are found to be similar, as discussed in Chapter 3, even though growth typically occurs in a different region of \(T-p_V\) space \([152]\). SPA studies indicate that the \((111)B\) surface-phase diagrams are also similar for OMVPE and MBE \([153]\).

The similarity of reconstructions observed for GaAs and InP layers grown by OMVPE and MBE is not surprising, based on the discussions of surface thermodynamics in Chapter 2. The surface reconstruction is determined by thermodynamic factors, so it is dependent only on the state parameters such as temperature and the group V partial pressure at the solid/vapor interface, as indicated in Figures 2.50 and 3.4. As discussed in Chapter 3, the surface reconstruction has major effects on aspects of the OMVPE growth process including growth rate, surface morphology, dopant incorporation, and microstructure.

\textbf{Reflection Difference Spectroscopy}

A surprising development in the use of RDS for the monitoring of the OMVPE growth process was the observation of oscillations during the LPOMVPE growth of \((001)\) GaAs \([154, 155]\). The oscillations are still not completely understood, but they apparently relate to a different RDS pattern between step edges and the \((001)\) terraces between steps \([156]\). The oscillations observed during growth by RDS and X-ray scattering are found to be closely correlated \([56]\).

Elegant fundamental studies have been performed for the CBE growth of Si and GeSi from disilane \([157]\) where RHEED and RDS (RAS) oscillations were
measured simultaneously. Of course, for the \((2 \times 1)\)-reconstructed \((001)\) Si surface, monolayer steps separate \((001)\) terraces having orthogonal rows of Si dimers. RDS was determined to measure the periodic variation in the domain coverage in monolayer by monolayer growth. Thus, the information obtained from RDS and RHEED is shown to be complimentary. For example, the RDS oscillations disappear for growth at low temperatures \(<550^\circ\text{C}\) where \(\text{H}\) passivates the dangling bonds on the dimerized surface. The \((2 \times 1)\) structure persists, so the RHEED pattern does not change, but the electronic structure of the dimers changes, eliminating the RAS oscillations.

The combination of spectroscopy during RDS with the use of the oscillations allows the \textit{in situ} measurement of growth rate, thickness, and solid composition for \textit{III/V} alloys [158]. \textit{In situ} monitoring of the surface reconstruction also allows a determination of the “efficiency” of various As and P precursors—that is, the surface reconstruction is measured versus the group V partial pressure and temperature [159]. The hydrides are found to be less efficient precursors than organometallic precursors such as TBAs and TBP. At low temperatures the partial pressure to obtain a specific reconstruction is higher for the hydrides than for the tertiarybutyl-substituted precursors. This is simply due to the more rapid pyrolysis of the latter, as discussed in detail in Chapters 4 and 5. RDS has also been shown to be capable of giving information about the doping type and level during OMVPE growth, which assists with the control of device structures [160].

\textbf{Surface Photo Absorption}

SPA is similar to RDS in that it typically measures the difference in UV reflectivity in orthogonal \((110)\) directions on the \((001)\) surface. The laser beam is incident in a direction normal to the surface for RDS. In SPA, the beam is incident at the Brewster angle to minimize bulk effects [161]. Since it is closely related to RDS, the results obtained using the two techniques are often similar. They have many of the same advantages and disadvantages (e.g., the determination of surface reconstruction using SPA is indirect, as for RDS). The phase diagram for As stabilized GaAs surfaces grown by OMVPE shows the same \((2 \times 4)\) and \((4 \times 4)\) structures seen for growth by MBE, as discussed in Chapter 3 and seen in Figure 3.4. SPA has also been used for the determination of the surface-phase diagram for InP grown by OMVPE [161], as discussed in Chapter 2 and seen in Figure 2.50.

SPA has the advantage over RDS in one important respect. Incidence at the Brewster angle minimizes bulk effects. For example, ordered structures in the solid, described in Chapter 2, break the symmetry in the solid so produce a bulk reflectance anisotropy at normal incidence [163] that is absent in SPA [164].

An extremely important use of SPA has been the study of the fundamental surface processes involved in OMVPE growth. As discussed in Chapters 3 and 5,
these heterogeneous processes are difficult to measure by conventional techniques. The change in surface reconstruction induced by introducing a group III or group V precursor into the system can be observed to study the surface pyrolysis processes of the group III [165, 166] and group V [167–169] precursors.

SPA can be used to monitor the OMVPE growth process in a manner similar to that described earlier for RDS. For example, it has been used to explain the basic processes leading to monolayer growth in the atomic layer epitaxy (ALE) process [170]. Even more important is the use of SPA to monitor the transients involved in compositional switching at heterostructure and quantum-well interfaces. This has been demonstrated for GaAs/GaInP system [169, 171]. The As/P exchange during InAs/InP (and GaInAs/InP) heterostructure growth, discussed in detail in Chapter 9, can also be monitored and controlled using SPA [169, 172]. This has led to the production of abrupt InAs/InP quantum-well structures “which could not have been made” without in situ process feedback using dynamic SPA analysis [173].

7.6.3 Total Reactor Pressure

The use of low pressures (10–80 Torr) is common in the large reactors described earlier to improve uniformity. This point is worth considering in more detail. The basic idea probably originates from the Si processing industry where low-pressure reactors are used to deposit uniform films of dielectric materials on large areas in a single run. The wafers can even be stacked in close proximity. However, the extension of this approach to the growth of high-quality, single-crystalline III/V semiconductors is tenuous. The basic idea of the low-pressure process for dielectrics is to use growth conditions dictating that the growth rate is limited by surface reaction rates rather than by mass transport. As the pressure is reduced, the diffusion coefficient is increased, as in Equation (6.5); thus, the mass-transport rate is increased. In addition, low substrate temperatures are typically used to reduce the rate of surface reactions. This allows uniform growth rates with little or no concern for hydrodynamic factors such as boundary layer thicknesses and so on. The key parameter controlling growth rate is the substrate temperature, since the process is controlled by the kinetics of the chemical reactions involved in growth. Thus, if the substrate temperature is uniform, good thickness uniformity and high reaction efficiency can be obtained, even for unusual geometries such as stacked wafers. However, it is unlikely that this approach will be applicable to the growth of single-crystalline semiconductors because the material quality is typically poor for growth in the kinetically limited regime.

Are there rationales for the use of low pressures in the midtemperature, mass-transport-limited regime? For the growth of GaAs, InP, GaInAs, and other alloys for which the growth information is fairly complete, low-pressure operation does not appear to be particularly beneficial for small-scale reactors where one to three
2'' wafers are processed per run. Certainly the use of low pressures will minimize convective eddy currents, but so will proper hydrodynamic design. This assumes that the trimethyl-group III precursors are used, thus avoiding parasitic reactions.

Even in small-scale reactors, when the triethyl-group III precursors are preferred, low-pressure operation is normally required to avoid parasitic reactions. At atmospheric pressure, premature reactions are significant and unavoidable using these precursors. The use of low reactor pressures will reduce or eliminate the problem. This has been well demonstrated for the growth of InP and GaInAs using TEIn and the group V hydrides. TEIn forms an adduct with both AsH₃ and PH₃ in the gas phase that partially pyrolyzes, forming a low-volatility polymer on the reactor walls upstream from the substrate. The reaction efficiency and uniformity are poor in typical atmospheric-pressure reactors but are perfectly satisfactory in low-pressure reactors. This is simply because given fixed input group III and group V molar flow rates, the number of gas-phase collisions experienced by each molecule before reaching the substrate is decreased as the reactor pressure is decreased. Thus, the reactions are more likely to be heterogeneous at lower pressures. This appears to be the prime motivation for the original use of low-pressure OMVPE reactors by Duchemin and coworkers [174].

The problems with homogeneous nucleation in the growth of ZnS (and ZnSe) using DMZn and H₂S (and H₂Se) are reduced at low reactor pressures, as discussed in Section 7.5, for exactly the same reasons: fewer gas-phase collisions produces a shift from homogeneous gas-phase reactions to heterogeneous surface reactions.

Low-pressure operation is typical and, indeed, may be required for large-scale reactors where the increased dimensions make recirculating currents and parasitic wall deposition nearly unavoidable at atmospheric pressure. An additional positive aspect of the use of low reactor pressures is that increased diffusion in the lateral direction (parallel to the substrate surface) improves the lateral homogeneity. This has been demonstrated over small distances [6]; however, it is not expected to be a major factor for large reactors.

Another suggested advantage of the use of low pressures is the increased selectivity of growth. At a total pressure of 1 Torr, GaAs is not nucleated on dielectric mask layers over a wide range of growth temperatures. At low pressures, complete homogeneous group III pyrolysis does not occur, so adsorption on the dielectric layer is weak, which prevents nucleation. On the GaAs substrate, adsorption is stronger, so nucleation and growth occurs selectively in the openings in the mask where the substrate is exposed. However, for most precursors selective growth occurs even in atmospheric-pressure reactors, as described in Section 8.9.

A negative aspect of the use of low pressures, in addition to the increased complexity of the reactor, is that the pyrolysis rates of the group V hydrides decrease, sometimes markedly, as discussed in Section 5.3.2, requiring the use of extremely high values of V/III ratio, frequently exceeding 100, in the input gas stream. This
is understandable in terms of our growth model. If the pyrolysis reactions were simple homogeneous, unimolecular processes, the fraction of the group V hydride molecules pyrolyzed would decrease simply because the pyrolysis rate is in the fall-off regime, as discussed in Chapter 5. In addition, the residence time in the hot region of the reactor, near the substrate, is decreased as the pressure is lowered. For the hydrides, the unimolecular process is frequently heterogeneous. In this case, the surface coverage is proportional to the partial pressure of the precursor, which decreases as the system pressure is reduced at a constant input molar flow rate. This also results in a decrease in the pyrolysis rate. In addition, surface interactions between the group III precursors and the group V hydrides are minimized. When this is the mechanism responsible for the low-temperature pyrolysis of the group V hydrides, the pyrolysis rate at low pressures will be reduced as a superlinear function of the total reactor pressure.

The extreme example of this problem is for CBE growth. In this case, for growth to occur at all, the group V pyrolysis must be assisted by an external cracking apparatus. Even the group III pyrolysis is a problem. The heterogeneous pyrolysis of TMGa, which occurs only when the AsH₃ is precracked to As and As₂, leaves the surface littered with CH₃ radicals. Thus, TEGa is typically used for the growth of high-quality GaAs by CBE. The same phenomena also lead to carbon contamination of GaAs grown in very low-pressure reactors.

Problems with carbon contamination are less severe for operation at atmospheric pressure for several additional reasons. The H₂ ambient itself plays a beneficial role by reacting with the trimethyl–group III precursors, as discussed in Section 5.3.1, removing the CH₃ ligands by forming CH₄ in the vapor phase. The H₂ also reacts directly with the CH₃ ligands produced by homolysis, again producing relatively inactive CH₄ molecules. Clearly, the use of low reactor pressures makes it more likely that CH₃ will reach the surface. In addition, without using much higher V/III ratios, the V hydrides will not produce the concentration of surface H required to eliminate the adsorbed CH₃ radicals before they can pyrolyze, leading to increased carbon incorporation into the lattice. The use of inert ambients can also lead to increased carbon contamination because they do not react with the CH₃ produced during pyrolysis of the cation precursors.

The most obvious disadvantage of the use of low reactor pressures is the expense of installing and maintaining the vacuum apparatus. Pumping reactive group III alkyls and group V hydrides is no simple matter. Even the quartz reactor itself must be more complex, as discussed in Section 6.5.

### 7.6.4 Precursor Molecules

Discussion of the optimum reactor configuration and pressure has continued for decades, since the inception of OMVPE. The range of source molecules considered was, however, originally severely limited since a limited range of precursor
7.6 Design of the Overall Process

materials could be obtained from the suppliers with the required purity. The rapid development of OMVPE for commercial-scale use in recent years has produced a dramatic change, as discussed in Chapter 4. Today, design of the OMVPE process has expanded to encompass the design of the precursor molecules themselves. We have discovered that organometallic chemists are capable of designing molecules with specific properties, including pyrolysis temperature, vapor pressure, toxicity, and more.

The triethyl-group III molecules suffer from prereaction difficulties, while TMIn has the disadvantage of being a solid at room temperature. The combination EDMIn, with a single methyl group replaced by an ethyl radical, is a liquid that has been discovered [175] to behave chemically in the OMVPE reactor similarly to TMIn. It is now available in electronic-grade purity and has been used to grow extremely high-purity InP [176]. Perhaps most dramatic has been the development of less hazardous group V organometallic molecules to replace the hydrides, as discussed in detail in Chapter 4. The most successful are TBAs and TBP. They are now used in production-scale operation [177, 178].

Te precursors such as MATe and DTBTe have been designed to have lower pyrolysis temperatures than the commonly available DETe and DMTe. Group VI molecules such as C₄H₄S and MSH are designed to pyrolyze at temperatures higher than for DMZn and DMCd, to retard homogeneous nucleation of the solid upstream from the substrate. Adduct group II precursors are used to retard parasitic reactions.

Selection of the optimum source molecules is frequently unrelated to the reactor pressure and geometry. In this case, the aspect of the process design related to the choice of source molecules is based on criteria such as toxicity, convenience (mainly vapor pressure, melting point, etc.), availability in high-purity form, and pyrolysis temperature, as described fully in Chapter 4. In addition, compatibility is sometimes a problem as in the growth of HgCdTe. The other major fundamental consideration is freedom from C contamination.

As the development of novel precursors has continued, it has now become common to use different precursors for different growth conditions, for particular reactor pressure and temperature. For example, TMAA is probably the most commonly used Al precursor for CBE, but parasitic reactions, including the exchange of alkyls with other group III precursors, occurs at higher reactor pressures where gas-phase collisions are frequent. As discussed in Chapter 4, special precursors have also been developed especially for low-temperature growth.

7.6.5 Optimum Growth Conditions

The choice of optimum growth conditions is an important aspect of the overall process design. The independent parameters such as substrate temperature, V/III ratio, total flow rate, substrate misorientation, and so forth are normally
empirically determined to give the desired materials properties—for example, the best morphology and highest purity. The range of parameters is constrained by fundamental considerations. For instance, the growth temperature is chosen to fall within one of the three regimes, defined in terms of the growth-rate-limiting mechanism, and to provide the optimum doping level and mobility. For normal processes, the mass-transport-limited regime is favored. For ALE, the kinetically limited regime is mandated. The V/III ratio for growth of III/V alloys is nearly always chosen to be \( \geq 1 \) due to the low volatility of the group III elements. The reverse is true for II/VI alloys where the II/VI ratio is often \( \geq 1 \), since the group II elements are volatile. The basic effects of V/III ratio on doping and defect formation were discussed in Sections 7.3 and, more extensively, in Section 2.4.3. However, the actual optimum values must be determined empirically. Unfortunately, they are not even constant for a given reactor. Changing a source bottle frequently requires a minor fine-tuning of the growth parameters. This will, hopefully, be eliminated or at least minimized using \textit{in situ} control, as discussed earlier.

We should also emphasize that the optimum conditions for one material will not be the same as for a different semiconductor. Even compounds as closely related as InP and GaAs, both grown using trimethyl-group III and hydride–group V sources, can be quite different. For example, higher growth temperatures are reported to give the highest-purity InP [175] and GaInAs [179] layers: the carbon concentration decreases with increasing temperature. This is opposite to the situation for GaAs, as previously discussed. The apparent dichotomy is a result of carbon incorporation being related to several processes: (1) adsorption/desorption of CH\(_3\), (2) the addition of atomic H to form CH\(_4\) that is immediately desorbed, (3) breaking down of CH\(_3\) before incorporation, and (4) the thermodynamics of incorporation. The first and second factors are expected to give less carbon at high temperatures, the third favors low temperatures, and the fourth produces a relatively minor effect [180], although the strong Ga-C and Al-C bonds, as compared with the much weaker In-C bond, make the In compounds generally easier to grow free of carbon. Another example is the growth of AlGaAs. Here high temperatures are required to allow desorption of Al suboxide from the surface. The higher volatility of the Ga and In oxides allows the desorption of these oxides at much lower temperatures.

### 7.6.6 Reactor Configuration and Safety

Finally, we arrive at the most practical considerations in reactor design, the actual configuration, packaging, and safety aspects. Even these aspects of reactor design are partially determined by fundamental factors. For example, glove boxes and vacuum interlocks are used to avoid exposing the internal quartz and graphite reactor parts to an atmosphere containing oxygen and/or water that adsorb on surfaces, causing severe problems for the growth of Al-containing materials such as AlGaAs and AlGaInP. In response to the desire to produce superlattice struc-
tures consisting of many layers, modern reactors are computer controlled. As described earlier, commercial reactors today are likely to have integral techniques for control of the process, including EPISON for control of the flows of the organometallic species, pressure controllers, and optical characterization apparatus for *in situ* control of the surface and the film being produced. In the future, the apparatus is bound to be less dependent on operator intervention, with automated wafer handling and operation.

Safety aspects of OMVPE are of great concern. As the OMVPE technique moves into production, the equipment is frequently used by nonexperts. Especially in this case, failsafe protection is required for the technicians and engineers as well as other users of the same air-handling system. A number of papers have described various strategies for dealing with the safety issues [181–185].

The table compiled by Hess and Riccio [183], included as a part of Table 4.6, demonstrates the level of danger associated with the use of the group V hydrides AsH$_3$ and PH$_3$. Compounding the hazard is the storage of the hydrides in high-pressure cylinders. Some laboratories prefer to use the pure hydride sources since the room-temperature vapor pressures, 12 atm for AsH$_3$ and 30 atm for PH$_3$, are much lower than for cylinders of the hydride diluted in H$_2$. In either case, the storage of the toxic gas cylinders in locked, vented gas cabinets adjacent to the reactor is required. Should the safety hazard be deemed lower for remote storage, welded, double-wall stainless steel tubing should be used to transport the gas to the reactor cabinet. An approach to minimizing the hazard, emphasized in earlier chapters, has been the replacement of the most hazardous precursors, the anion hydrides, by less toxic, liquid organometallic precursors. TBP and TBAs are the leading candidates. Not only are these materials less toxic, but they are also more slowly dispersed, which adds a factor of approximately 100 to their safety relative to the hydrides. They also ignite upon exposure to air. A serious leak in the TBAs line in my laboratory resulted in a pile of As oxide on the floor of the reactor. The toxic gas alarms were not even activated. The leak acted like the jet in a carburetor, promoting immediate oxidation of the TBAs. This is not to say that these materials are absolutely safe. The same safety procedures used for the hydrides must be employed. Fortunately, common toxic gas monitors used for detection of the hydrides respond to many of these materials as well.

The reactor should be enclosed in a cabinet that is held at a pressure slightly below that of the room to minimize escape of gases into the room in the event of an accident. In many commercial-scale reactors, the outer reactor is made from stainless steel, which helps prevent catastrophic accidents that can occur owing to fracture of the quartz in a typical laboratory-scale reactor. Additional precautions frequently employed include: (1) monitoring of gas storage cabinets for release of toxic gases using appropriate detectors; (2) hydrogen alarms to guard against fire hazards and also to detect leaks in the toxic gas lines, since the hydrides are frequently diluted in H$_2$; (3) additional toxic gas detectors installed inside the reactor housing, the gas handling system, the exhaust system, and the room occupied by
the operators; and (4) external alarms and monitoring of the toxic gas levels from outside the reactor room.

Modern practice calls for flow-limit valves on each toxic gas cylinder to prevent release of the entire contents of the cylinder in a short time due to an error or failure of some component of the system. Cross purge-vent assemblies are used to allow thorough purging of toxic gas from the regulator and line before opening the line to change cylinders. Most computer-controlled systems also have an emergency interlock system that shuts the toxic gas valves in the event of loss of air flow or electric power or when gas levels exceed the preset toxic gas alarm level.

In some laboratories the safety precautions have extended to the use of self-contained rooms, remotely observed and operated [184]. The room exhaust is purged through a dedicated system with continuous monitoring for toxic gases with the room maintained at a negative pressure.

In all cases, the most effective measures involve common sense as well as appropriate safety apparatus. Constant care and vigilance are required for the safe use of OMVPE equipment. In my laboratory, the first precaution is a rule that at least two people must be present—the buddy system. Several pairs of self-contained breathing apparatus are located outside of the laboratory. We also have breathing apparatus attached to large air cylinders for use during the most dangerous processes, such as the changing of cylinders or otherwise working inside the reactor cabinets. Another excellent idea is the use of a flashing red light outside the laboratory to warn unauthorized personnel not to enter the room. Naturally, dry chemical fire extinguishers and eye/face wash and body showers are located in the immediate vicinity of the OMVPE laboratory.

An area that generates considerable disagreement is the handling of the reactor exhaust. Charcoal drums have commonly been used to collect the unreacted hydrides in past years. The potential for explosion and/or fire from the large quantity of adsorbed pyrophoric material stored in large drums is a potentially serious problem. Some systems bleed oxygen or water into the charcoal drum for controlled oxidization of the hydrides. Others add oxygen to the exhaust and controllably oxidize the organometallic and hydride products to form the less hazardous oxides. It should be remembered that the arsenic oxides are carcinogenic. Another popular approach is simply to heat the exhaust in a quartz tube to well above the temperature required for pyrolysis to deposit the waste as a solid. The remaining exhaust can then be burned or passed into a charcoal drum. The resultant materials generated from each of these approaches is handled as solid toxic waste.

References


References