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KINETIC ASPECTS IN THE VAPOUR PHASE EPITAXY OF III–V COMPOUNDS

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Successful exploitation of the unique properties of III–V compound semiconductors has resulted in development of several new devices for optoelectronic and solid state microwave applications. These achievements, however, would not have been possible without major advances in the technology for epitaxial growth of such materials. Further improvements in device performances together with new applications of III–V compounds must be closely coupled with even more progress toward achievement of material with properties approaching the theoretical values. Chemical vapour deposition has emerged as the most common technique for epitaxial growth. Although significant improvements can be obtained through empirical methods of investigation of such processes, it is recognized that in the long run a firm fundamental understanding is essential. This realization provides the motivation for detailed, basic studies of the kinetics and thermodynamics of epitaxial growth by chemical vapour deposition. This review will examine the progress, both past and projected, in measurement and interpretation of the kinetics of vapour phase deposition of III–V epitaxial layers. The scope will be limited to near-atmospheric pressure, open flow epitaxial systems utilizing chemical transport. To date, most of the studies have concerned GaAs, GaP, InAs, InP, and their alloys. It has been demonstrated for GaAs, and for some of the other compounds as well, that, depending on the growth conditions, epitaxial deposition may proceed in two fundamentally different rate-limiting regimes. At low temperatures the rate is limited by a surface process; while at higher temperatures mass transport limitations appear to prevail. For mass-transport-limited deposition the sensitivity of the growth rate to various operating parameters can, in many cases, be predicted from theoretical considerations. Investigation of kinetically limited growth offers a path toward a fundamental understanding of the atomistic surface events that result in epitaxial growth. The progress in these areas will be discussed; in addition, experimental and theoretical tasks for future studies will be recommended.

1. Introduction

Chemical vapour deposition is now established as the most widely employed approach for epitaxial growth of the III–V compound semiconductors. In many cases development of new semiconductor devices based on the unique properties of these materials was achieved only after major advances in the technology for vapour epitaxy. As is often the case with compound semiconductors, each stage of progress required the support of relatively fundamental investigations. This has resulted in a considerable body of basic data related to the vapour deposition processes; indeed, the amount appears to be disproportionate when compared with silicon vapour epitaxy. The kinetic studies are widely dispersed in the scientific and engineering literature; yet taken as a whole, they provide a solid foundation for future investigations, which may lead to detailed discriptions of the actual atomistic events that proceed on the substrate surface during vapour phase epitaxy. In the present study an effort will be made to consolidate the findings to date and to assess the present state of understanding as applied to vapour phase epitaxy of III–V materials. The discussion will be limited to near-atmospheric pressure, open flow, chemical vapour deposition processes.

Both scientific and commercial motivations exist for kinetic studies of III–V vapour epitaxy. With respect to the former, there are a number of features which make the processes highly attractive experimental vehicles for study of epitaxial growth in general. The most common III–V processes are exothermic and consequently deposition proceeds within a hot-wall apparatus. This feature simplifies not only the experimental rate measurement technique but also the interpretation of the resulting kinetic data. Important clues can be obtained relating to the growth mechanisms of compound materials by investigating the influence of the gas phase composition on the growth kinetics. Polar surfaces resulting from the noncentrosymmetric

crystal structures of III–V materials permit examination of epitaxial growth on surfaces with ideally identical atomic geometries and packing densities but with greatly different chemical properties. Solid solutions over wide composition ranges are formed between various III–V compounds; hence, deposition of alloys can be a fruitful area for study. The composition of the solid being epitaxially deposited as related to the gas phase composition is becoming a major area of endeavor. Vapour deposition of III–V compounds can proceed under conditions such as that deposition occurs only on the substrate surface and not on the substrate holder and other extraneous parts of the apparatus even though all are at the same temperature. Thus, it may be considered that under these conditions, the deposition process is catalyzed by the substrate surface. In fact, epitaxial growth can be an excellent vehicle for studying the fundamental nature of heterogeneous catalysis in general. The catalysis surface is relatively well defined, being a single crystal, and the extent of reaction is easily measured since a portion of the reaction products remain on the catalyst or substrate surface. These are only a few of the features that facilitate and motivate kinetic studies of III–V materials.

From an economic point of view the kinetic results are applied to optimization of yield and deposition efficiency. Successful scale-up of these deposition processes in conjunction with ever increasing levels of automation requires a firm fundamental understanding of the kinetic factors in order to assess the sensitivity of the rate to various operating parameters. Improved epitaxial layer properties such as surface quality, crystal perfection, and the electrical and optical characteristics can be associated with a better understanding of the basic nature of the deposition events. In the following sections the results of accumulated thermodynamic and kinetic investigations will be summarized. The interpretation of these results will be discussed in terms of possible rate-limiting regimes and deposition models.

2. Thermodynamic analyses

Fundamental to investigation of any chemical vapour deposition process is a thorough thermodynamic or equilibrium analysis. It is, of course, naive to expect quantitative agreement between the extent of deposition calculated from thermodynamic considerations and that experimentally measured in open flow, epitaxial systems. The thermodynamic considerations are strictly applicable to equilibrium conditions, which can be approached only by operating a deposition process at rates that are generally too slow to be practical. Instead, with typical systems the gas velocities and reactant residence times are such that only a portion of the gas stream has an opportunity to equilibrate with the substrate. Furthermore, as will be shown, the surface processes (i.e., adsorption, surface reaction, desorption, etc.) may be too slow to permit reactant equilibration. Thus practical processes are usually mass-transfer or kinetically limited. Nevertheless, even under these rate-limiting conditions, thermodynamic analyses provide important information. For example, the extent of gas phase supersaturation under which deposition is occurring may be calculated. The stability and relative concentrations of various species can be estimated and the limiting temperatures for deposition ascertained. In some cases the composition of alloy deposits may be predicted.

In general, with the exception of the limited use of organometallic pyrolysis systems, III–V vapour epitaxial processes use halide transport of the group III element. Although iodine transport was popular in the early days of III–V epitaxy, chloride transport has emerged as the method of choice. In a classic paper Fergusson and Gabor [1] presented a thermodynamic analysis of the Ga/As/I/H and Ga/As/Cl/H systems. A table of thermodynamical data compiled from the literature or estimated for the gaseous and solid species of interest became the basis for a large number of subsequent calculations. Later Hurle and Mullin [2] described the results of a generalized set of calculations for the Ga/As/Cl/H system. The data were presented in a form suitable for prediction of the feasibility of GaAs epitaxial deposition from various input gas compositions. The thermochemical data used in these calculations came principally from Fergusson and Gabor with the exception of the values of the standard enthalpies of formation for GaAs(s), As_4(g) and As_2(g), which were taken from a review by Thurmond [3]. Selection of thermochemical values for use in equilibrium calculations determines to a great extent the validity of the results. Consequently, with almost every new set

of calculations, the old values are reassessed and any newly determined values are considered. Compilations of thermochemical values for the III–V compounds have appeared [4–6].

Equilibrium calculations have been reported for deposition of several discrete III–V compounds, among these may be cited: GaAs [1, 2, 7–13], GaP [14–16], and InP [13, 17]. In general, the calculations show that processes using halide transport are exothermic and, as such, the extent of deposition is expected to increase as the deposition temperature is reduced. For GaAs growth using a hydrogen carrier the principal gaseous species are GaCl, HCl, As_4 and As_2, regardless of whether the original source of arsenic is AsH_3, As, GaAs or $AsCl_3$. The possible existence of $GaCl_2$ or Ga_2Cl_4 has been debated. Although its presence has been suspected or detected in hydrogen-free systems [18], it has generally been assumed to be absent under ordinary deposition conditions in a hydrogen ambient. Ban [19] was able to experimentally demonstrate the absence of $GaCl_2$ by monitoring in situ the gas phase composition in the deposition region using mass spectroscopy in conjunction with capillary sampling. Using transpiration techniques. Battat et al. [20], found $GaCl_2$ to be present at temperatures below 900 K, which are well below the normal deposition temperatures.

A number of thermodynamic analyses of epitaxial deposition of solid solutions of III–V compounds exist. Among these may be cited the following: $Ga_xIn_{1-x}As$ [21–25], $Ga_xIn_{1-x}P$ [26, 27], $GaAs_xP_{1-x}$ [28, 29], $Ga_xAl_{1-x}As$ [30], and $InAs_xP_{1-x}$ [25, 70]. Such calculations permit determination of the equilibrium composition of the deposit as a function of the vapour composition or the composition of a condensed alloy source.

Since epitaxial III–V deposition from halide transport systems requires a condensed source composed of solid III–V compounds or liquid group III metals, interpreation of a thermodynamic analysis requires consideration of the equilibria associated with the source. This is particularly true for the widely employed $Ga/AsCl_3/H_2$ process for GaAs deposition where the source is initially liquid gallium; however, prior to epitaxial growth it becomes covered by a crust or film of GaAs. The existence of this crust must be recognized in analysis of the equilibria associated with the $Ga/AsCl_3/H_2$ deposition system [12, 31, 32].

3. Kinetic data

Reliable kinetic studies of open flow, CVD epitaxial growth are hindered by the large number of operating variables associated with these systems. It is difficult to isolate effects due to a single variable. For example, most of the III–V processes require source transport, and investigations of deposition rate as a function of flow rate are complicated by variations in source transport rate or efficiency due to the same flow rate variations. Fortunately, it is possible to avoid most of the problems by judicious selection of the experimental approach, e.g., use of source processes, such as the reaction of HCl with Ga, that have been demonstrated to operate at close to 100% efficiency [19, 33]. Care must be exercised in measurements of deposition rate as a function of substrate temperature to ensure that the source temperature and, hence, its transport rate remains constant. Extraneous deposits, which may form on the walls of the reactor or the substrate holder, can lead to irreproducible rate data by competing with the substrate for reactants with subsequent depletion of the incoming gas stream. Fortunately, with many III–V epitaxial processes the deposition is rather selective over a wide range of conditions and is essentially confined to the substrate surface. Under certain growth conditions the deposition rate will be a strong function of the crystallographic orientation of the substrate. Variations in substrate surface orientation of a few degrees can dramatically alter the rate. Consequently, the surface orientation must be accurately ascertained and reported together with the experimental results.

In the conventional method of measurement the growth rate is computed by dividing the observed deposit thickness by the accumulated time of deposition during a single run. Proper use of this approach, however, requires that a series of depositions be made for various time intervals under otherwise identical conditions to determine if the deposit thickness is a linear function of time. It has been demonstrated that under some conditions the deposition rate may change with time [34]. An approach that permits detection and evaluation of rate variations in a given deposition run is to periodically introduce small amounts of dopant impurities into the gas stream [35–38]. After deposition the layer is sectioned and etched to reveal differences in electrical characteristics within the deposit caused by the intentional changes in gas phase

dopant concentration. These changes thus serve as time markers and allow evaluation of the growth rate as a function of time. A more precise technique [39] consists of gravimetrically measuring the growth rate continuously as the layer is deposited by suspending the substrate from a recording electrobalance as illustrated in fig. 1. The electrobalance, which continuously monitors the weight of the crystal during deposition, is protected from corrosive reactants by a hydrogen counterflow. By electronically differentiating the balance output voltage as a function of time the actual deposition rate is monitored. The system is sensitive to rate changes of 0.003–0.005 μm/min. Such continuous rate monitoring systems are more precise and rapid than conventional techniques. Furthermore, effects due to small variations in substrate properties are eliminated because many experiments can be conducted on the same substrate. Gravimetric techniques have been applied to investigation of GaAs [31, 39, 40] and InAs [41] epitaxial growth.

In addition to precise rate measurements, knowledge of the actual vapour composition present in the deposition region is essential for proper interpretation of the kinetic results. Usually this composition is inferred from experimental source transport measurements and thermodynamic considerations. However,

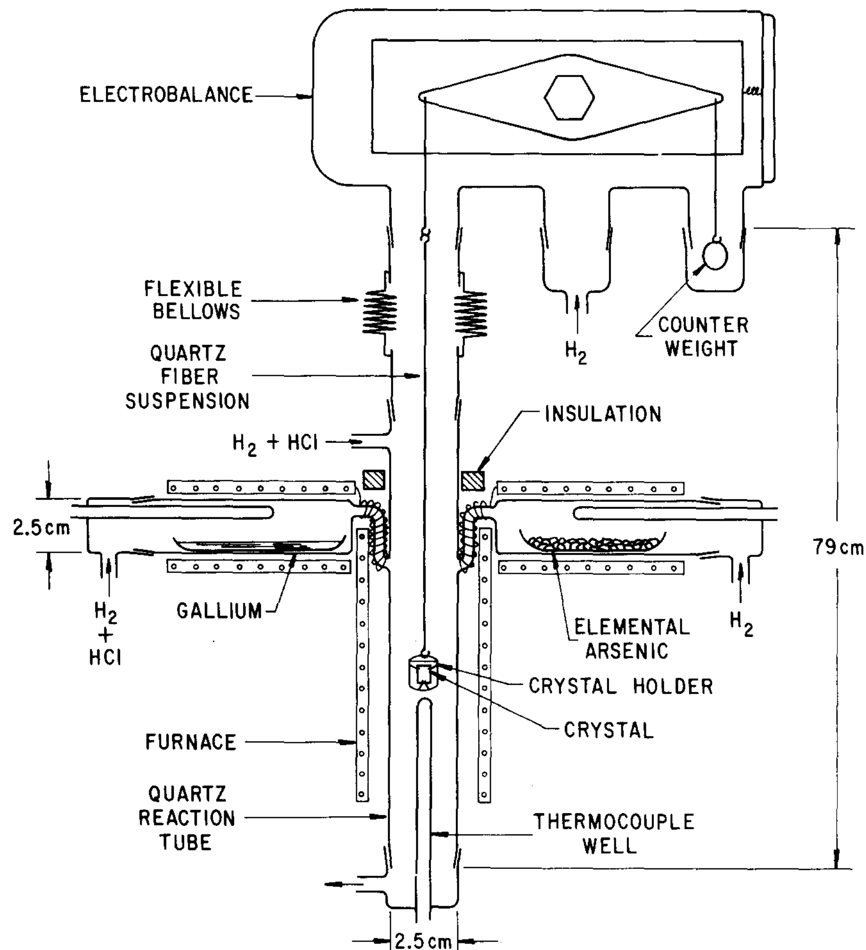


Fig. 1. Gravimetric system for continuous growth rate measurement during epitaxial growth [39] (with permission of the Electrochemical Society).

Ban [19, 42, 43] has demonstrated that in situ measurements can be obtained by coupling a mass spectrometer to the reactor through a small quartz capillary. Although, as yet, this continuous method of vapour composition analysis has not been combined with a continuous rate monitoring system; the results should be very beneficial.

It is well known that the rate of a CVD epitaxial process can be determined by either material transport or surface events or a combination of both. This is a result of the serial nature of the steps leading to epitaxial growth. Transport of reactants to the deposition region by the flowing gas stream, transfer within the deposition region of reactants between the bulk gas stream and the substrate surface by diffusion or free convection, and the surface processes of adsorption, surface reaction and desorption are series steps. If one step is inherently slower than the others, it will determine the overall deposition rate. Depending on the rate-determining step, CVD epitaxial processes can be categorized as mass transport limited, mass transfer limited, or kinetically limited (see ref. [44] for a more detailed discussion of these limitations). In the mass-transport-limited category are included processes where the reactant residence times within the deposition region are of sufficient duration to permit equilibration of essentially all entering reactants with the substrate. Such processes are rarely encountered in open flow, CVD epitaxy of III–V compounds. The rates of mass-transfer-limited (also called diffusion limited or mass transport limited – Type II) processes are determined by the rate of transfer of reactants or products between the substrate and the bulk gas stream through some stagnant region. The transfer occurs via gas phase diffusion or convection, both of which are physical processes. Finally, kinetically limited processes exhibit rates which are determined by a chemical event such as adsorption or surface reaction that either involves the surface as a reactant or takes place upon it.

The rate-limiting regime in which an epitaxial process is operating can, in principle, be ascertained from measurement of the deposition kinetics as a function of temperature, flow dynamics, substrate orientation, etc. In general, determination of the rate-limiting regime(s) must be the principal initial objective of any kinetic study. In the remainder of this section the experimental data available for III–V deposition will be discussed with this objective in mind.

Thermodynamic analyses show that the extent of GaAs deposition using halide transport should decrease with increasing substrate temperature. This behavior was indeed observed in early investigations [8, 9, 45]. Evidently, the range of investigated temperatures was limited in these studies; and it has subsequently been verified by many investigations [12, 18, 31, 33, 39, 46–51] that two distinct regions of temperature behavior exist. At higher temperatures the thermodynamically predicted behavior is observed and the rate increases as the temperature is lowered; however, with additional temperature reduction the rate passes through a maximum and then begins to decrease as illustrated in fig. 2. The high temperature rate behavior is qualitatively similar to that predicted from thermodynamic considerations; but, quantitatively, the absolute rates are far below those expected for complete equilibration [33]. This is indicative of a mass-transfer-limited process which will be discussed in more detail later. At low temperatures the rate increases rapidly with

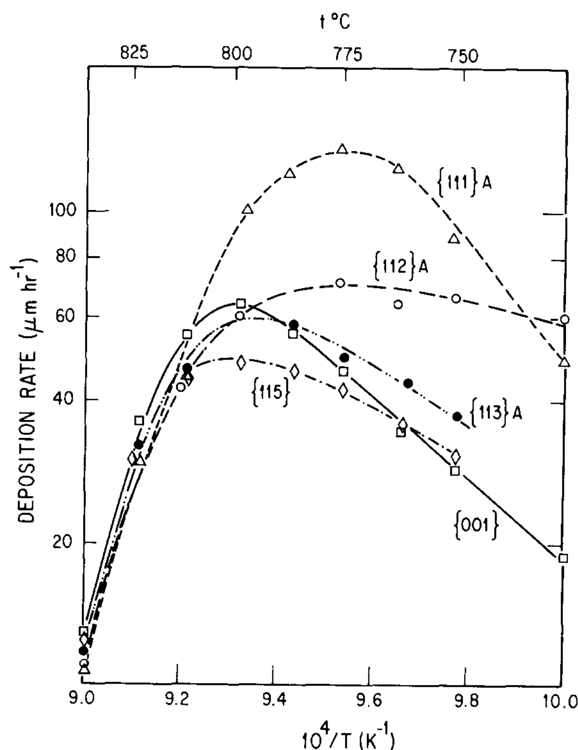


Fig. 2. Effect of substrate temperature on GaAs epitaxial deposition rates for various crystallographic orientations. Data from ref. [33].

increasing temperature. This activated behavior is characteristic of chemical reactions and is opposite to that expected from thermodynamic considerations. In the low temperature region the process must operate in a kinetically limited regime. This contention will be supported with additional evidence below. The activation energies calculated from the low temperature slopes of the rate versus reciprocal temperature curves obtained by different investigators are in good agreement as shown in table 1.

These values for GaAs may be compared with values for {001} oriented deposition of $GaAs_xP_{1-x}$ (190 kJ mol^{-1}) [53] and InAs (230 kJ mol^{-1}) [41]. Examination of fig. 2 reveals that the curves for various orientations have different slopes in the low temperature region and, hence, different activation energies. This is evidence that the nature of the rate-determining kinetic step differs with the crystallographic orientation of the surface. In some studies [33,39] the {111} B or {111} As deposition rate has been found to be almost independent of temperature. As yet the significance of this observation is not understood.

The influence of substrate orientation on the GaAs growth kinetics has been widely investigated [9, 18, 33, 35, 46–51, 54–59]. From fig. 2 it can be seen that sizeable differences exist among the growth rates of different surface orientations in the low temperature region. This is additional support for the conclusion that the process is kinetically limited at low temperatures. At higher temperatures fig. 2 shows that the differences diminish and the rates for all orientations tend to converge. The rates in this region may be interpreted as being mass transfer limited and, as such, are not influenced by events occurring on the substrate surface. Low temperature deposition rates for major low and high index orientations are illustrated in fig. 3 with

Table 1
Activation energies for {001} GaAs epitaxy

System	E_a (kJ mol^{-1})	Reference
$GaAs/AsCl_3/H_2$	200	Calculated from [52]
$Ga/HCl/As/H_2$	200	[39]
$Ga/AsCl_3/H_2$	170	[12]
$Ga/AsCl_3/H_2$	200	[31]
$Ga/AsCl_3/H_2$	190	[49]

two sets of rate data taken from independent investigations. In one study [58] the rates were measured by simultaneous deposition on variously oriented substrate slices; while in the other [35] the data were obtained by deposition on a hemispherical substrate using the cyclic doping technique described earlier. Although different vapor compositions were used in the two studies, the results are in fair agreement. In general, local rate minima are found on the plot at orientation positions corresponding to the more densely packed surfaces. The existence of a local minimum at {111} could not have been detected in the slice-by-slice investigation unless a very large number of high index surfaces were studied. On the other hand, this is readily revealed by growth on hemispherical substrates since all orientations are simultaneously exposed to deposition. Although the two sets of data displayed in fig. 3 are in reasonable agreement, examination of the literature reveals that, unlike the effects of substrate temperature, substrate orientation effects differ widely from investigation to investigation. Most studies find that the rates are very sensitive to the crystallographic orientation at low temperatures, but large differences are observed in the relative rates of various orientations [60]. These discrepancies most likely result from the fact that the rates for each orientation are different functions of the vapour composition. For example, it has been demonstrated that the relative growth rates of the {111} A and {111} B orientations can be inverted by varying the gas phase stoichiometry under which the deposits are being formed [33, 55]. Thus the {111} A rate decreases with increasing gas phase Ga/As mole ratio while the {111} B increases. In general, the value of data on growth rate as a function of crystallographic orientation is severely diminished without accompanying information on the vapour composition employed in the deposition. For III–V materials other than GaAs limited kinetic data with respect to crystallographic orientation exists. Likewise there is little information on the influence of substrate orientation on the composition of mixed III–V alloys deposited under kinetically limited conditions.

If the growth rate at low temperatures is kinetically limited, then the rate should be independent of the gas flow dynamics. This observation has been experimentally verified at least at higher flow rates [31, 33, 46, 52]. The effect is illustrated in fig. 4 where the total flow rate and thus the gas velocity was increased three-fold

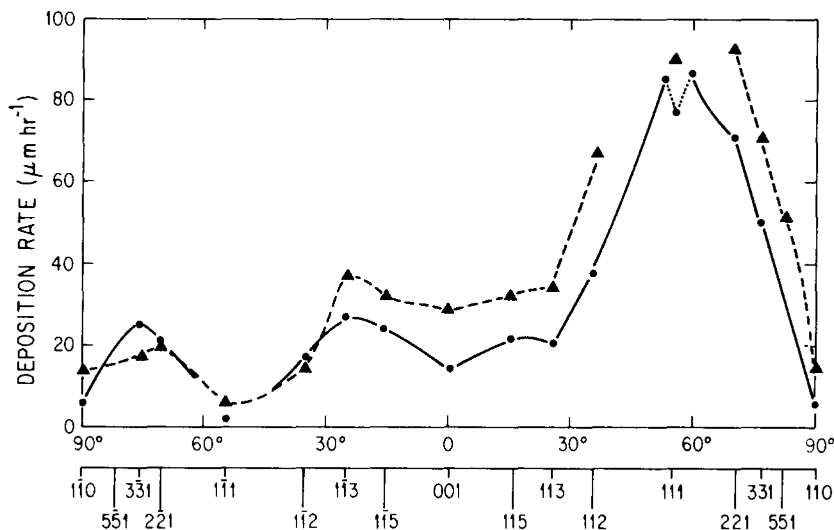


Fig. 3. Gallium arsenide deposition rate as a function of crystallographic orientation. Abscissa represents deviation of substrate surface orientation in degrees from (001): (▲) data from ref. [58] (deposition temperature 750°C); (●) data from ref. [35] (deposition temperature 755°C).

without significant variations in the {001} deposition rate.

The influence of vapour composition on the GaAs deposition rate has been studied in detail for the {001} orientation [39]. A gravimetric rate measurement system was employed and the effects of the initial arsenic and gallium monochloride partial pressures were studied as a function of substrate temperature. The variation of the growth rate with increasing initial arsenic partial pressure is illustrated in fig. 5 for several substrate temperatures. By examination of the rate–temperature behavior it is possible to ascertain which portions of the curves in fig. 5 were taken at low temperatures under kinetic limitations. The rate is found to be a slowly

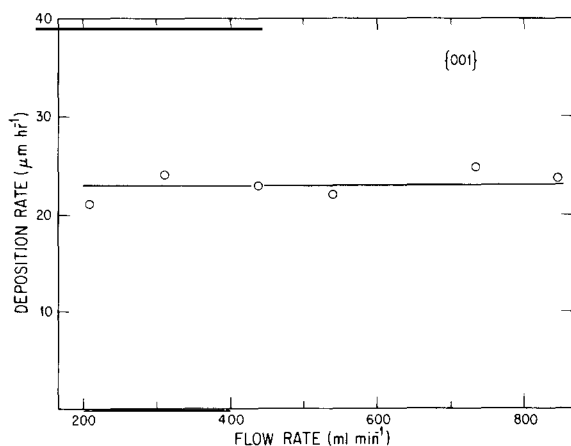


Fig. 4. Effect of total flow rate on GaAs epitaxial deposition rate at 750°C. Data from ref. [33].

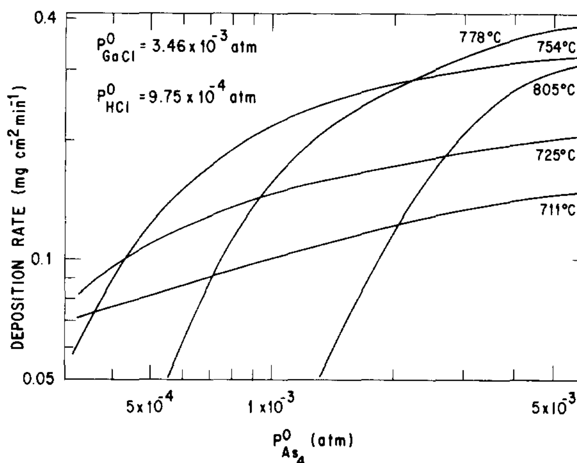
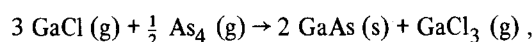


Fig. 5. Gallium arsenide {001} epitaxial deposition rate as a function of arsenic initial partial pressure at several substrate temperatures. After ref. [39].

increasing function of the initial arsenic partial pressure when kinetically limited. If the arsenic partial pressure is held constant, the growth rate increases as a function of the initial gallium monochloride partial pressure. However, at low temperatures, the opposite is found; the rate actually decreases as the gallium monochloride partial pressure is increased [39, 61]. This behavior is illustrated in fig. 6. Examination of rate–temperature curves [39] reveals that the inverse dependence of rate on gallium monochloride partial pressure occurs when the process is kinetically limited. A similar behavior is found for InAs deposition [41]. As will be discussed in the next section, this observation is an important clue to the nature of the deposition mechanism.

In halide transport systems two overall reactions leading to deposition have been assumed. Using GaAs as an example, these are disproportionation,



$$3\,\mathrm{GaCl\,(g)} + \tfrac{1}{2}\,\mathrm{As_4\,(g)} \rightarrow 2\,\mathrm{GaAs\,(s)} + \mathrm{GaCl_3\,(g)}\,,$$

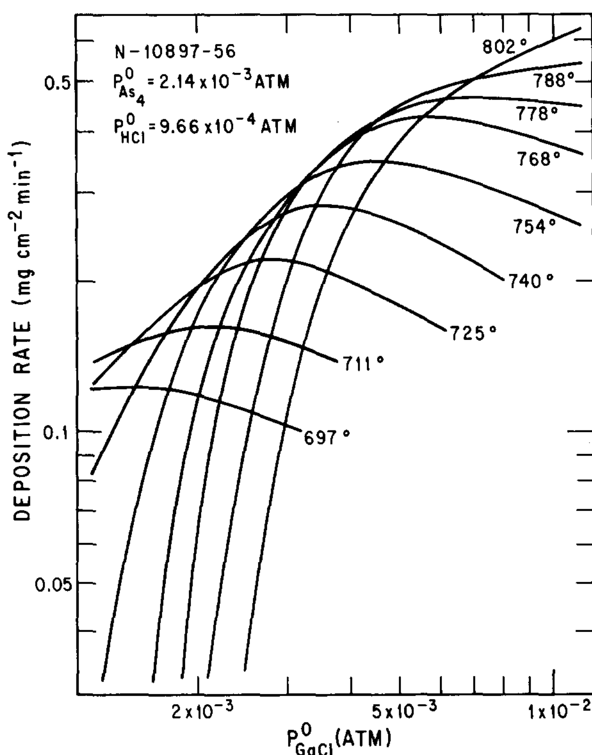
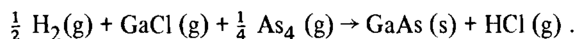


Fig. 6. Gallium arsenide {001} epitaxial deposition rate as a function of gallium monochloride input partial pressure at several substrate temperatures [39] (with permission of The Electrochemical Society).

and reduction,



$$\tfrac{1}{2}\,\mathrm{H_2(g)} + \mathrm{GaCl\,(g)} + \tfrac{1}{4}\,\mathrm{As_4\,(g)} \rightarrow \mathrm{GaAs\,(s)} + \mathrm{HCl\,(g)}\,.$$

Thermodynamic analysis [12] shows that when hydrogen is used as a carrier gas reduction should be favoured, the deposition equilibrium being promoted by the large excess of H_2. In addition mass spectroscopy [19] of the by-products in the deposition zone revealed only HCl with no $GaCl_3$. On the other hand, processes using Ar or N_2 as a carrier likely proceed via disproportionation with the trichloride being formed as a reaction product [18, 62].

In alloy deposition the formation of mixed group V vapour species such as As_xP_y or As_xSb_y has been detected [63]. The relative stabilities of the various mixed species may influence the composition of $GaAs_xP_{1-x}$ and $GaAs_xSb_{1-x}$ formed at different temperatures from a given initial gas phase composition. The kinetics of GaN deposition are determined to a large extent by a slow homogeneous process, the decomposition of NH_3. Although from an equilibrium point of view NH_3 should dissociate in the reaction zone, it is found to exist principally in a metastable, nondissociated state [43, 64]. It is suspected that $GaCl_3 \cdot NH_3$ is an intermediate species in the deposition of GaN with a Ga/HCl/NH_3 system.

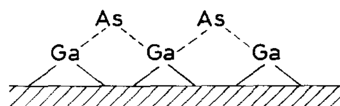
4. Models and mechanisms

In development of predictive models and atomistic mechanisms, identification of the rate-limiting regime under which the kinetic data was obtained becomes crucial. If the process is mass transfer controlled, models can be derived to describe the fluid dynamics and mass transfer characteristics of the system. Such models become very beneficial in optimizing the deposition efficiency as well as the uniformity in physical properties of the layers. In a kinetically limited regime the kinetic data can be used to develop and test possible surface deposition mechanisms.

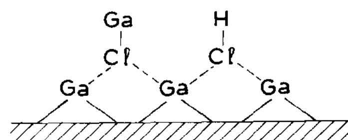
At high temperatures (such as those above the rate maximum in fig. 2) many halide-transport III–V epitaxial processes exhibit rate behavior that is consistent with a mass-transfer-limited regime. It is commonly assumed in such cases that the surface processes are so rapid that reactants reaching the substrate surface are able to react to the extent that the equilibrium partial

pressures exist there. The difference between the reactant partial pressures at the surface (equilibrium values) and those in the bulk gas stream (input values) becomes the driving force for mass transfer. A useful approach to modeling this state of affairs is that proposed by Sedgwick [65]. The flowing gas stream is divided into two hypothetical portions, one of which is assumed to equilibrate with the substrate while the other passes by unreacted. The fraction (Sedgwick's β) of the gas stream that equilibrates is determined empirically from the ratio of the experimentally measured amount of deposition to that computed for complete equilibration from thermochemical data. The value of β is dependent on the fluid dynamics and the transfer characteristics of the molecular species. Once determined, it is useful for prediction of deposition rates only for a given set of gas stream velocities and reactor-substrate geometrical configurations. This approach does, however, permit computation of the rates as a function of the reactant input concentrations. For a typical GaAs deposition process a value of $\beta = 0.09$ was obtained [39]. In order to describe the effects of reactor geometry and fluid dynamics in mass-transfer-limited III–V deposition, a considerably more complex model is required. The finite element technique has been applied to GaAs deposition with success [66]. Although the calculations are complex and require a large scale computer solution, they can be applied without making assumptions with regard to a boundary layer shape and thickness.

At low temperatures under kinetically limited conditions the rate data may be used to obtain information concerning the basic surface steps which determine the epitaxial deposition rate. In principle, the atomistic growth mechanism can be ultimately resolved. At the present, this goal has not been achieved; however, the foundation has been formed. Most of the efforts have concentrated on GaAs epitaxy because of the considerable amount of kinetic data available for this material. As described in the preceding section, the GaAs growth rate increases rather slowly as a function of the arsenic input partial pressure. On the other hand, when kinetically limited, the rate is inversely proportional to the gallium monochloride partial pressure at high input values. The rate is also inhibited by addition of HCl to the reactant gas stream. These observations suggest a competitive adsorption process with GaCl and HCl molecules competing for the available arsenic adsorption sites on the {001} surface. This may be illustrated by the following simplified diagrams:



arsenic adsorption,



GaCl or HCl competitive adsorption.

The Ga–Cl–Ga bridges present in the competitively adsorbed complexes are well known in gallium chemistry [67]. Since the sites occupied by GaCl and HCl are unavailable for arsenic adsorption, the growth rate must be retarded by increased partial pressures of these species in agreement with the observed behavior. If we assume that As_4 is in gas phase equilibrium with As_2 and that the latter adsorbs dissociatively on the {001} surface as depicted above, then for a Langmuir-type adsorption process, the fraction of the surface covered by adsorbed arsenic is given by

$$\theta_{As} = \frac{K_{As_2}^{1/2} P_{As_2}^{1/2}}{(1 + K_{As_2}^{1/2} P_{As_2}^{1/2} + K_{GaCl} P_{GaCl} + K_{HCl} P_{HCl})} .$$

Now if the molecularity of the rate-limiting surface step is greater with respect to adsorbed arsenic than with respect to the other reactant, GaCl, then the rate will decrease with increasing gallium monochloride or hydrogen chloride partial pressure whenever

$$K_{GaCl} P_{GaCl} \gg 1 + K_{As_2}^{1/2} P_{As_2}^{1/2} + K_{HCl} P_{HCl} ,$$

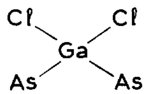
or

$$K_{HCl} P_{HCl} \gg 1 + K_{As_2}^{1/2} P_2^{1/2} + K_{GaCl} P_{GaCl} ,$$

where K_i refers to the Langmuir adsorption coefficients of the subscripted species. Unfortunately, these coefficients have not been determined. In fact, there is little information available on reactant adsorption isotherms for GaAs surfaces. Kirovskaya and Ustalova [68] have studied the adsorption of GaI_3, H_2, and their mixtures on {311} and {111} (polarity undesig-

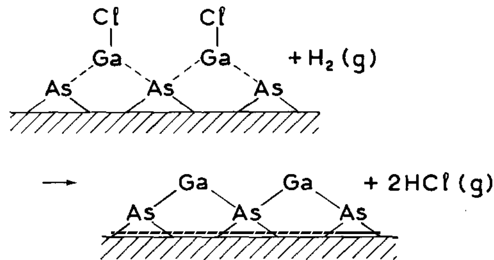
nated) GaAs surfaces. It was concluded that GaI_3 adsorbs selectively on Ga atoms. Although this result applies to different orientations from {001}, it illustrates adsorption of a gallium halide onto surface gallium atoms.

Geometrical analysis of surface adsorption complexes is another approach to interpretation of the kinetic data. It may be particularly useful in accounting for rate variations between different surface orientations. On the basis of such an analysis, Loyau [69] has proposed the formation of an absorbed surface complex,

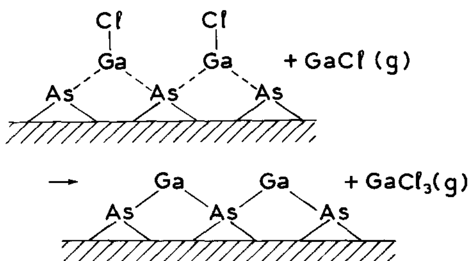


during GaAs epitaxy. In order for layer-wise crystal growth to proceed, it is necessary to desorb the chlorines which would tend to poison the surface.

Several plausible mechanisms may be proposed which involve competitive adsorption. For example, two adsorbed GaCl molecules on adjacent sites can undergo reduction according to the following scheme:



The above step would be followed by arsenic adsorption to continue the process. In the absence of a hydrogen ambient,disproportionation as a result of the approach of another gaseous GaCl near the same surface complex may be more likely. This may be represented by



which would also be followed by arsenic adsorption to continue the process. Such mechanisms are, of course, highly simplified. More detailed mechanisms must take into account the two different ⟨110⟩ directions on a {001} surface and should consider the possibility of surface reconstruction. Possible mechanisms can, in principle, be tested with the kinetic data. In fact, the reduction process described above, when combined with the competitive adsorption concept, yields a rate expression that is in qualitative agreement with the experimental results. However, quantitative comparison is limited due to the unknown adsorption coefficients and kinetic rate constants. Additional progress in this area requires more experimental data.

5. Summary and recommendations

As a class the III–V semiconductors have been the object of a considerable amount of fundamental studies relating to their vapour phase epitaxial deposition. As might be expected the bulk of these activities have concerned GaAs; however, other materials such as InP, GaN, InAs, and $GaAs_xP_{1-x}$ are receiving increasing attention. Several thermodynamic analyses of III–V vapour deposition provide the fundamental basis for additional experimental endeavors. These analyses are limited by the accuracy of the thermochemical values upon which they are based. Existing values have, in several cases, been subjected to considerable recent revision as more experimental data is accumulated. Nevertheless, for many compounds of interest only estimated values are available and additional experimental investigations are greatly needed.

A considerable kinetic data base has been accumulated at least for {001} GaAs vapour epitaxy from chloride transport systems. Depending on the temperature and vapour composition the deposition may proceed under two fundamentally different rate-limiting regimes. One of these is kinetically limited and kinetic studies under these conditions provide insight into the basic surface processes that occur during deposition. Effects associated with competitive adsorption of reactants on specific surface sites are evident and the possible nature of the adsorbed complexes have been examined. For additional understanding of the surface mechanisms leading to epitaxial growth, detailed, self-consistent kinetic data for the other principal crystallographic orientations are

required. This should be particularly fruitful with respect to the two polar {111} surfaces. Kinetic behavior similar to GaAs has also been demonstrated for InAs and $GaAs_xP_{1-x}$. As yet the kinetic data on these materials are limited, but as the data base accumulates, it should be possible to evaluate the effects of atomic substitution, e.g., indium for gallium, iodine for chlorine, or phosphorus for arsenic. The possibility of substitutions such as these and the kinetic effects which they produce make the III–V semiconductors extremely artractive experimental vehicles for study not only of vapour phase epitaxial growth but also heterogeneous catalysis and vapour–solid interactions in general.

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