

Bangor University

DOCTOR OF PHILOSOPHY

The kinetics of GaAs MOCVD using in situ Laser Reflectance Monitoring

Clayton, A.J.

Award date: 2005

Awarding institution: University of Wales, Bangor

Link to publication

General rights Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
You may not further distribute the material or use it for any profit-making activity or commercial gain
You may freely distribute the URL identifying the publication in the public portal ?

Take down policy If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

The Kinetics of GaAs MOCVD using *In Situ* Laser Reflectance Monitoring

A thesis submitted to the University of Wales in candidature for the degree of

Doctor of Philosophy

By

A.J. Clayton

University of Wales, Bangor 2005





Contents

1.0	Introd	luction1						
	1.1	Development of MOVPE2						
	1.2	Thermodynamics of MOVPE4						
	1.3	Compar	Comparison of MOVPE with other growth techniques5					
	1.4	GaAs as	GaAs as a device material7					
	1.5	<i>In situ</i> n	In situ monitoring techniques					
	1.6	Aims	Aims					
	1.7	Referen	References12					
2.0	Litera	ure review14						
	2.1	Decomposition of TMGa and AsH ₃ 14						
		2.1.1	<i>In situ</i> infi	rared spectroscopy monitoring of reaction products 15				
		2.1.2	2 In situ mass spectroscopy to monitor reaction products					
		2.1.3	Existing investigations into the reaction mechanism for					
			GaAs dep	osition22				
	2.2	Existing	g MOVPE investigations in process reactors					
		2.2.1	2.2.1 Importance of reactor design					
		2.2.2	2.2.2 Large scale manufacturing in MOVPE					
		2.2.3	2.3 Time dependent model of mass transfer of gas phase species31					
		2.2.4	2.4 Gas flow patterns					
		2.2.5	5 Factors affecting the growth rate					
		2.2.6	2.2.6 Relative effects of parasitic growth and reactor temperature					
		distribution39						
	2.3	Modelli	ing kinetic-limited GaAs deposition45					
		2.3.1	Surface reactions from TMGa and AsH ₃ 46					
		2.3.2	Multi-step reaction model of gas phase and surface reactions 51					
			2.3.2.1	(110)-surface54				
			2.3.2.2	(111)-Ga surface				
			2.3.2.3	(100)-surface misoriented towards (110)57				

i

			2.3.2.4 Simulation of GaAs growth by MOCVD57				
	2.4	Summar	ry				
	2.5	References					
3.0	Exper	imental a	nd theoretical model62				
	3.1	Gas syst	as system6				
		3.1.1	Experimental parameters				
	3.2	In situ re	eflectance monitoring72				
		3.2.1	Absolute reflectance model75				
	3.3	Analytic	cal techniques82				
		3.3.1	X-ray diffraction				
		3.3.2	Scanning electron microscopy (SEM) and energy dispersive				
			X-ray spectroscopy (EDX)				
		3.3.3	Atomic force microscopy (AFM)				
		3.3.4	Inductively coupled plasma – atomic emission spectroscopy				
			(ICP-AES)				
	3.4	Theoret	ical model				
		3.4.1	Steady state approximation (SSA)92				
	3.5	Referen	ces95				
4.0	Result	s and disc	discussion				
	4.1	Experin	nental results				
		4.1.1	Reflectance data produced from deposition experiments96				
		4.1.2	Comparison of reflectance data with the absolute				
			reflectance model103				
		4.1.3	Surface morphology of deposit grown under different				
			conditions107				
		4.1.4	Crystal orientation in deposit116				
		4.1.5	Nucleation time and growth rate118				
		4.1.6	ICP-AES analysis of the total deposit produced in				
			experiments121				

ii

	4.2	GaAs yield results using theoretical model123			
		4.2.1	Model 1		
		4.2.2 Model 2			
			4.2.2.1	Surface MMGa128	
			4.2.2.2	Surface Ga130	
			4.2.2.3	Surface AsH131	
			4.2.2.4	Surface As133	
	4.3	Carbon incorporation into GaAs135			
	4.4	Model using He in replace of H ₂ as carrier gas 140			
	4.5	Summary143			
	4.6	References144			
5.0	Conclu	sion and further work145			
	5.1	Conclus	ion		
	5.2	Further	work		
	5.3	Reference	ces		
Appendix 1					
Appendix 2 153					

iii

Acknowledgements

I would like to thank Prof. Stuart Irvine for his support and guidance throughout the last four years while I was researching this PhD project.

Many thanks to my family who have given me huge support emotionally and financially throughout the last 4 years, and have never doubted my decision to take on this PhD.

I would like to acknowledge the technical help I've had from Steve Jones, Mike Lewis and John Charles, as well as John Sambrook who sadly passed away during my PhD. Also, I would like to thank John Cambridge for carrying out the AFM analysis and Andy Davis who gave assistance with the SEM. I would also like to thank members of the research group, including Dr. Vincent Barrioz and Eurig Jones who have given technical and analytical assistance, allowing collection of results.

Messer Nippon Sanso supplied the arsine cylinder free of charge and with out it no experiments would have been done at all, so many thanks to them. My PhD was funded by EPSRC, including IQE who were my industrial sponsor. Without the financial support I would not have been able to undertake my PhD, so I am grateful for receiving the grant and the sponsorship over the three years.

Also, thanks to Dr. Dan lamb and Ceri Evans for proof reading my thesis, and to mention that their suggestions were taken onboard.

Summary

The kinetics of gallium arsenide (GaAs) parasitic growth during metal-organic chemical vapour deposition (MOCVD) was investigated using in situ laser reflectance monitoring. Experiments were carried out in a horizontal quartz reactor tube using trimethylgallium (TMGa) and arsine (AsH₃), with a reactor pressure of 200 mbar and total flow (F_{tot}) of 1.49 standard litres per minute (slm). A quartz wafer was aligned with the laser to allow the growth rate to be measured during growth. Experiments were carried out between 400°C and 500°C where surface reactions limit the growth rate. The V/III ratio was varied between 10, 30 and 50 by changing the partial pressure of TMGa (p_{TMGa}), while the AsH₃ partial pressure (p_{AsH_3}) was kept constant. The growth rate was observed to increase with temperature and p_{TMGa}, which was determined to be due to the increased supply of methyl radicals and concentration of gallium species at the surface. Reflectance oscillations were only obtained when coalescence of the growing deposit occurred at a greater rate than vertical growth. The 2-dimensional layer growth was observed at 450°C when the V/III ratio was equal to 10 and when both parameters were at high values in the range employed. Analysis on the surface morphology established that the reflectance intensity reduced when 3-dimensional growth occurred, with high intensity and the presence of oscillations when deposition was 2-dimensional. Compositional analysis determined that the parasitic deposit was non-stoichiometric, with an average Ga:As ratio of 1:(1.3). A kinetic model was developed using the steady state approximation and rate parameters obtained from the literature for the reaction mechanisms involved in the GaAs process. The model results correlated with the experimental results such that GaAs yield increased with temperature and p_{TMGa}. The measured growth rate from experiments was generally greater than that calculated in the model, which is expected to be due to the rough surfaces where a larger surface area increased the rate.

1.0 Introduction

The area of research reported in this thesis considers a GaAs metal organic vapour phase epitaxy (MOVPE) process using trimethylgallium (TMGa) and arsine (AsH₃). This is a technique used in the optoelectronics and semiconductor industry for the production of device materials. Such device materials are grown in a reactor (as described in the following pages), on a substrate where deposition occurs under controlled conditions. The principal problem associated with this process is that material is deposited in non desirable areas of the reactor. This may occur on the reactor walls, and is referred to as parasitic growth.

Parasitic growth is a result of thermal conduction from the heated susceptor to the reactor walls, where low temperature deposition occurs with the growth rate limited by surface reactions. This ultimately changes the conditions within the reactor chamber making control of the process growth environment difficult. Accurate control of the deposition conditions is paramount for producing abrupt interfaces to allow specific device operation. Drift of the required reactor parameters leads to a change from the acceptable device characteristics, reducing the commercial production for that device. The reactors thus have to be shut down so that they may be cleaned before production can continue. The many parameters that need to be controlled within a small, acceptable, drift range can vary between reactor shut downs.

The study of parasitic growth has been carried out by depositing GaAs using TMGa and AsH_3 in a horizontal quartz tube reactor, as described in Chapter **3.1.1**. The growth rate of the GaAs or Ga/As-containing material on the surface of the reactor walls and central quartz wafer was monitored in *situ* by laser interferometry, which measured reflectance variation due to changes in thickness and to the deposit surface during deposition.

This Chapter will introduce MOVPE and some other techniques used in the industry and lead on to discuss some investigations into kinetic-limited growth of GaAs, as well as existing studies on parasitic growth in a commercial reactor manufactured by Aixtron.

Existing models for GaAs epitaxial deposition are reported and then applied to parasitic growth of GaAs. Additionally, a kinetic model is presented, which was developed using rate parameters from the literature (discussed in Chapter **2.3.2**) on the gas phase and surface reactions of TMGa and AsH₃, and then compared to the experimental data. It is anticipated that the model could be applied to any horizontal reactor without being influenced by reactor geometry.

1.1 Development of MOVPE

The growth of semiconductors by MOVPE was developed towards the end of the 1960s by Manasevit [1.1]. Manasevit introduced metal-organic compounds and Group V hydrides over a heated substrate, at a temperature of around 700°C, and they reacted to produce epitaxial compound semiconductor layers. The investigation was a progression from the discovery of organometallic compounds in 1849 by Edward Frankland, who was studying methyl and ethyl radicals. His aim was to isolate the ethyl group from ethyl iodode with zinc. The reaction produced an ethyl zinc iodode compound, which was a liquid at room temperature and readily formed a vapour with a pyrophoric nature. Later, in the same Century (1891), Mond and Langer purified crude nickel at 50°C in carbon monoxide and formed nickel carbonyl, before transporting and decomposing it at 100°C [1.2].

Manasevit [1.1] used organo-Ga compounds such as triethylgallium (TEGa) and trimethylgallium (TMGa) due to their volatile nature, even at room temperature, making it possible to meter appreciable quantities of these compounds by bubbling a carrier gas through them. These compounds were mixed with different arsine (AsH₃), phosphine (PH₃), or mixed hydride concentrations that are controlled independently by simple flow-meter adjustments. The metal-organics are generally liquids at room temperature and a carrier gas is used which flows through the bubbler holding the liquid, to transport the vapour to the reactor. Control of the carrier gas flow through the liquid enables accurate and reproducible delivery of the metal-organic precursor, which can be further controlled by the temperature and thus the vapour pressure of the source [1.2].

TMGa has greater volatility than TEGa and was considered by Manasevit [1.1] to allow the deposition procedure to be more manageable. The accurate control of molar fractions of the precursors enabled the production of materials with specific properties. Devices have strict structure requirements for thickness, composition, impurity content and interface characteristics, including the need for uniformity of these characteristics over the whole of the deposition area. The manifold of the MOVPE gas system can quickly direct the precursors to the reactor chamber for the growth process, or bypass it straight to the exhaust, the so called vent/run system. Therefore, abrupt surface changes may be produced because the concentration of each species in the reactor can be controlled and rapidly changed. Stainless steel tubing with welded metal-to-metal fittings are needed for a clean and oxygen-free environment for growth and because the precursors are highly reactive and toxic in nature. The precursors mix in the reactor growth chamber and may initially decompose in the hot region above the substrate on the heated susceptor. Deposition also occurs on the reactor walls due to heat radiation from the susceptor [1.2].

Figure 1.1 illustrates the growth process in MOVPE in the reactor chamber. It shows epitaxial deposition where growth may occur at steps on the substrate surface, or when species nucleate to form islands of reacting species. The surface becomes 3-dimensional with island formation and as they increase in size they coalesce to form a smoother, 2-dimensional surface.



Figure 1.1: Epitaxial growth at steps and islands in the MOVPE process.

1.2 Thermodynamics of MOVPE

MOVPE deposition occurs because the system is not at equilibrium between the vapour phase of the input gas and the solid phase at the substrate. The thermodynamic driving force of the process is to restore equilibrium, which is when the concentration of the reacting gas phase species is equal to the concentration at the substrate for the specific growth temperature. This can be referred to as the chemical potential, μ , of each phase. Under process conditions, the chemical potential of the gas phase, μ_g , is greater than that of the solid phase, μ_s . The difference of the two chemical potentials, $\Delta\mu$, represents the thermodynamic driving force to restore equilibrium. The amount of deposit to establish equilibrium is the maximum amount of solid that can be produced under the given conditions. In such circumstances, the growing surface is referred to as supersaturated. The observed growth rate under process conditions is generally lower than that required for the system to reach equilibrium due to individual growth processes [1.3]. The growth process can be considered as diffusion of reacting gas phase species to the solid interface (substrate), and subsequent surface reactions.

Under process conditions, where the gas has large supersaturation, $\Delta \mu_g > 0$, near equilibrium can exist at the gas-solid interface, where surface reactions are fast. There is little difference between the chemical potential of the diffusion of gas species ($\Delta \mu_d$) and that of the reaction of species at the surface ($\Delta \mu_s$). Under these conditions $\Delta \mu_d \leq \Delta \mu_s$, the kinetics of both processes can be considered to occur at the same rate. At low temperatures non-equilibrium of the system occurs at the solid interface, typically at temperatures below 550°C for GaAs deposition from TMGa and AsH₃. The gas is considered as an infinitesimally small volume over the substrate and its partial pressure to be at near equilibrium with the gas-solid interface [1.4]. Investigations of the individual processes limiting the growth process are discussed in Chapter 2.3.2. The thermodynamics of a system can determine the solid composition for growth in MOVPE. The gas phase is generally considered to be ideal, where

$$\mu_{i} = \mu_{i}^{0} + RT \ln \frac{P_{i}}{P_{i}^{0}}.$$
(1.1)

The chemical potential of the ith component is μ_i , represented by μ_i^0 at equilibrium of the system, R is the gas constant, T is the temperature and P_i is the partial pressure of the ith component, with P_i⁰ referring to the partial pressure at equilibrium. The solid phase has a non-ideal part to which has to be considered,

$$\mu_{i} = \mu_{i}^{0} + RTln(a_{i}).$$
(1.2)

The non-ideal part, a_i , is the activity which is the product of the concentration, x_i , and the activity coefficient, γ_i . Models have been developed to calculate the activity part of μ , such as the Regular Solution model and the Delta Lattice Parameter (DLP) model [1.3].

1.3 Comparison of MOVPE with other growth techniques

As well as MOVPE, there are a number of other crystal growth techniques for the production of epitaxial structures for compound semiconductor devices, such as liquid phase epitaxy (LPE), molecular beam epitaxy (MBE), and more recently chemical beam epitaxy (CBE) [1.2]. The MBE process uses evaporation of solid and elemental sources under low pressure, below 10⁻⁴ Torr, with a background pressure of approximately 10⁻¹⁰ Torr, so that growth can occur without gas phase interactions. In Gas Source MBE (GSMBE), a hydride gas is used in replacement of solid Group V sources. CBE uses a hydride and metal organic gas source as in MOVPE, whilst still adopting the beam nature of MBE. MOVPE, MBE and CBE are the major epitaxial techniques for the production of electronic devices.

Using GSMBE to grow heterostructures, consisting of multiple layers of variable compound materials, is challenging due to a large flux of hydride evaporated from the Group V solid source, with switching between different precursors by shutter operation making control of input concentration difficult. Up scaling to multiwafer reactors can be problematic, with difficulty in control over compositional grading of small thickness

layers, up to 100 nm. The multiwafer reactors also have large capacity evaporation cells that limit a rapid change of flux. Frequent material calibrations are needed for GSMBE because of changes of source surface area and cell temperature profile with material consumption. Scaling up with GSMBE to multiwafer reactors is also costly due to the increase of the cell capacity and the increased source to substrate distance. The process has also suffered from producing devices with poor performance and high defect density. MOVPE and CBE multiwafer equipment remains compact and simple [1.5].

CBE has low material consumption relative to MOVPE, which uses large amounts of toxic gases. CBE thus has advantages of purchase, storage and waste management of precursor gases, helping to reduce cost while benefiting the environment. Selective area epitaxy is also more straightforward with CBE, the surface has to be masked in areas where growth is not wanted in MOVPE. MOVPE can, however, cope with high volume production of devices, such as light emitting diodes (LEDs) and solar cells, more so than CBE [1.6]. One area CBE has difficulty with is the growth of aluminium-based semiconductors. Aluminium sources have not been suited to the CBE technique, because they need to be highly pure and are easily contaminated by oxygen leading to the formation of oxygen-rich micro-precipitates, which increase the total defect density significantly for alloys such as AlGaAs. Reloading sources in MBE and CBE is also very costly, more so for MBE. The techniques use ultra high vacuum (UHV) in the growth chamber, which needs to be vented to enable change of the crucible or cells. The chamber then needs to be baked and degassed, increasing the downtime of both processes [1.7].

The first commercial use for MOVPE was the production of a photocathode device, which worked using a thin GaAs/AlGaAs heterostructure bonded to glass to form a transducer that is fed into an amplifier and emits electrons onto a phosphor screen for viewing. MOVPE achieves the required limitation of surface defects and has been the only technique used in production of this device. The role of MOVPE in the optoelectronics market has increased over the last few years. In particular, LED manufacturing using MOVPE has increased significantly [1.7].

Until 1996, LPE and VPE were the major growth technologies for LED production. GaP green and AlGaAs high brightness red LEDs were mainly produced by LPE and the GaAsP:N orange, yellow and light green LEDs were produced by VPE. The move from indicators and simple indoor displays to more powerful signalling such as traffic signals and road signs required increased power efficiencies, and this can be achieved by MOVPE. Laser diodes (LDs) are produced by several industries. Simple long wavelength LD structures are produced by LPE, which is a low cost and well-established technology. MOVPE and MBE cover the more complex device structures using AlGaAs, particularly in CD applications. AlGaAsP LDs are only produced by MOVPE, thus increasing its usage in the optoelectronics market. AlGaAs grown on Ge substrates is manufactured exclusively by MOVPE for the solar cell industry for space applications [1.8]. Other III-V alloys, such as InGaAsP 1.3 µm wavelength LDs, are produced by MOVPE for optical fibre telecommunications.

1.4 GaAs as a device material

GaAs has been used in many device structures, often as a layer in a heterostructure where III-V alloy materials are deposited on GaAs substrates for applications such as lasers and LEDs. GaAs substrates can be manufactured with relative ease in comparison to the III-V alloys. The III-V alloys have to be deposited on GaAs templates. The growing alloy crystal structure can be lattice matched to GaAs, reducing strain effects that may cause structural dislocations, which affect the performance of the manufactured device [1.4].

GaAsP alloys were developed in the 1960s for production of red-LEDs, which were produced by liquid phase epitaxy (LPE), a technique that was reasonably well developed at this time. The following emergence of MOVPE, and related techniques such as MBE and CBE, led to more complex alloy structures, such as vertical-cavity surface-emitting lasers (VCSELs). The newer techniques were more versatile and suited to mass production. The AlGaAs/GaAs structure has been used for a range of devices, including

lasers, LEDs, high electron mobility transistors (HEMTs) and solar cells. LEDs in particular have depended upon III-V alloys, the AlGaAs/GaAs structure was used for red-LEDs, replacing the GaAsP structure, and AlGaInP/GaAs was used for yellow-LEDs. However, improved efficiencies of LEDs have resulted in GaAs being used less in the III-V alloys, as it can absorb some of the emitted photons.

GaP substrates have been found to be more transparent in the visible spectrum and have replaced GaAs substrates for some applications. The use of GaAs in electronic switching devices was at one time considered as an appropriate replacement to silicon (Si) in circuitry for computers. This was due to the high speed and low power consumption of GaAs relative to Si. Production of Si though was more cost effective than GaAs circuit production and has maintained its use in the industry. GaAs has replaced Si in the communications industry, where customer demands for pagers and cordless/mobile phones make cost less of an issue. Integrated GaAs circuits can deliver two to four times the speed and consume half the power of Si.

The use of GaAs in many applications within the semiconductor and optoelectronics industry demonstrates its commercial value as a device material. The applications described above are some examples of its use commercially where MOVPE has been used to produce device material structures and achieved the required performances for the industry [1.4].

1.5 In situ monitoring techniques

Many *in situ* characterisation techniques have been employed for MOVPE and other processes to develop and increase understanding of growth mechanisms in order to establish optimum growth conditions and enable reproducible quality of device materials. MOVPE is generally carried out at atmospheric or low pressure (several Torr), for which optical monitoring diagnostic tools are well suited. The surface is monitored using photons, which reflect with interfering wavelengths from the growing

film to a detector. Real-time growth information can be achieved, allowing immediate changes to the conditions to be made for optimisation of the process.

A number of techniques have been used to monitor epitaxial growth of GaAs. Kobayashi *et al.* [1.9] developed a surface photo-absorption (SPA) monitoring system in a MOVPE reactor in order to measure the GaAs growth process by Atomic Layer Epitaxy (ALE). The technique used P-polarised light with incidence at 70° to the surface, the Brewster angle for GaAs. This minimized the contribution from the bulk material to the total reflection and allowed the method to be sensitive to small changes at the surface. This technique is unsuitable for a typical MOVPE process where multiple layers are grown due to the small changes in the reflected light. However, the principle of optical monitoring is the same. Two optical windows were used to accommodate the angle of the probe, with a window flow of hydrogen flowing into the chamber. The window flow prevents deposition that may block the optical access. Figure 1.2 shows the experimental set-up.



Figure 1.2: Horizontal MOVPE reactor with the SPA monitoring system, after Kobayashi *et al.* [1.9].

Ellipsometry was a technique used by Lee and co-workers [1.10] to monitor GaAs MOVPE on GaAs (001) substrates, in a commercial Emcore Discovery 75 reactor using TEGa, TMGa and AsH₃. The probe was a 632.8 nm He-Ne Laser, also positioned at the Brewster angle. Oscillations were obtained and reported to correspond to monolayer growth with each period. The oscillations were observed to decrease with an increase of TEGa supply. The growth rate was also evaluated by determining the layer thickness after deposition. A linear dependence on TEGa supply was observed, with agreement to within 1% being reported between growth rate data obtained from *ex situ* thickness measurement, and that derived from the oscillation period assumed to be equivalent to a monolayer.

A similar technique to ellipsometry is laser interferometry. The advantage of this monitoring set-up is that near normal incidence to the substrate may be employed. This allows easier optical access with less restriction on the reactor configuration, which may affect the process when complex reactor design is required. Irvine *et al.* [1.11] investigated the growth kinetics of II-VI MOVPE with laser interferometry using a horizontal rectangular reactor. Growth rates were measured *in situ* from the laser reflection, which allowed measurement of growth rate change due to variation in temperature, concentration and VI/II ratio during the process. The changes in growth rate observed *in situ* with the variable conditions during the process gave insight into the mechanism involved in the II-VI growth chemistry.

Weeks *et al.* [1.12] followed on from the research of Bergunde *et al.* [1.13], and used *in situ* laser interferometry to monitor AlGaAs MOVPE of VCSELs in a planetary Aix-2400 8 x 3 susceptor multiwafer reactor. There was no optical access facility in the reactor design. This was overcome by replacing an existing thermocouple port with a quartz rod to act as an optical guide. This was fixed over the wafer toward the outside edge. The incident beam was near normal to the wafer surface and had to pass through the quartz liner at the ceiling where parasitic deposition had been reported [1.13]. The diode laser used [1.12] was 50 mW, with a wavelength of 980 nm, which had been

proven to penetrate parasitic deposit from initial experimentation. The investigation was aimed towards monitoring both the epitaxial and parasitic deposition simultaneously.

Using results reported by Bergunde *et al.* [1.13], the temperature range at the ceiling was expected [1.12] to be between 300 and 500°C. Interferograms were obtained during buffer layer growth in a reactor with an existing parasitic deposit from previous runs. High reflectance oscillations were obtained due to the parasitic deposit including a periodic variation in reflection at a higher frequency, which appeared as noise on the oscillatory curve. The periodic response of the high frequency reflection corresponded to the planetary rotation speed [1.14]. This signal was attributed to the wafer surface from the periodic nature between the reflection from the wafer surface and the non-reflective graphite susceptor (or planet). Also, greater reflectance had been observed [1.12] from the wafer surface relative to the quartz top plate. The observed reflectance can be seen in Figure 1.3.



Figure 1.3: Typical interference oscillations generated from parasitic deposition on a quartz top plate, after Weeks and co-workers [1.12].

Initial parasitic growth rate starting in a clean reactor was observed to be greater than the rate once a parasitic deposit had been established. The rate was reported to be constant for the remainder of the buffer layer growth. It was found, however, that the presence of

a thick deposit on the quartz top plate of the Aixtron reactor after a series of growth runs attenuated the reflected signal from the substrates. The conclusion from the investigation was that the parasitic growth process can't be explained purely by a temperature-limiting growth model. This was due to the fact that there was similarity between the growth rates at the quartz ceiling and the wafer surface, even though there had been a large temperature difference between the two positions. It was expected that gas phase and surface reactions had to be significant as well.

1.6 Aims

This study will describe the findings from experiments carried out using *in situ* laser interferometry and will discuss the results with the following aims:-

- 1. To establish what major reaction mechanisms are involved between TMGa and AsH₃ from a kinetic model using Arrhenius parameters reported in the literature.
- 2. Imitate conditions used in the Aixtron planetary reactor and carry out experiments with *in situ* laser interferometry measurements, varying parameters such as temperature and V/III ratio.
- 3. Determine layer composition and morphology using *ex situ* analysis of deposits grown on quartz slides within the reactor tube.
- 4. Relate the *in situ* and *ex situ* analysis with the process model.

The following chapter discusses previous investigations of the GaAs MOVPE growth process, and looks at existing models of the deposition mechanism for development of the quantitative model reported in Chapter **2.3.2**.

1.7 References

^[1.1] H.M. Manasevit, W.I. Simpson; J. Electrochem. Soc. 116 (1969) 1725.

^[1.2] M.A. Tischler; *IBM J. Res. Develop.* **34** (1990) 828.

- [1.3] G.B. Stringfellow, J. Crystal Growth 68 (1984) 111.
- [1.4] "Organometallic Vapour-Phase Epitaxy: Practice and Theory", G.B. Stringfellow, Academic Press, 2nd Edition (1999).
- [1.5] F. Alexandre, J.L. Benchimol, P. Launay, J. Dangla, C. Dubon-Chevellier; Solid State Electronics 38 (1995) 1667.
- [1.6] E. Veuhoff; J. Crystal Growth 188 (1998) 231.
- [1.7] J. Ch. Garcia; J. Crystal Growth 188 (1998) 343.
- [1.8] R.L. Moon, J. Crystal Growth 170 (1997) 1.
- [1.9] N. Kobayashi, T. Makimoto, Y. Yamauchi, Y. Horikoshi, J. Crystal Growth 107 (1991) 62.
- [1.10] J-S. Lee, S. Sugou, Y. Masumoto, Japn. J. Appl. Phys. 38 (1999) 614.
- [1.11] S.J.C. Irvine, J. Bajaj, J. Crystal Growth 145 (1994) 74.
- [1.12] K.J. Weeks, S.J.C. Irvine, S. Bland, J. Crystal Growth 257 (2003) 116.
- [1.13] T. Bergunde, F. Durst, L. Kadinski, Yu.N. Makarov, M. Schafer, M. Weyers; J. Crystal Growth 145 (1994) 630.
- [1.14] K.J. Weeks, S.J.C. Irvine, A. Stafford, S. Jones, S. Bland, A. Joel, Mat. Sci. and Eng. B 80 (2001) 46.

2.0 Literature review

2.1 Decomposition of TMGa and AsH₃

Early work on the chemistry of TMGa and AsH₃ reactions in a static system was carried out by Ring and Schlyer [2.1]. AsH₃ was heated over a silicon film for 2 hours at 265° C, 275 Torr, and no decomposition was observed. At 172°C and 219 Torr, AsH₃ was introduced into the reactor over a GaAs film, approximately 6% AsH₃ was consumed with production of H₂. This was evidence for the catalytic nature of GaAs for AsH₃ decomposition. Likewise, TMGa was introduced over a GaAs surface at 257°C at 37 Torr for 75 minutes and approximately 7% TMGa was consumed producing nearly half as much CH₄ [2.1].

Previous work [2.2] showed that the introduction of TMGa over an arsenic film at 245°C and 300°C at 175 Torr produced no CH_4 , although variable amounts of TMGa were consumed, demonstrating that TMGa decomposition occurred in one form or another. The reaction of TMGa and AsH₃ was investigated by heating the reactants at 203°C for 240 minutes or 259°C for 75 minutes at varying pressures over a GaAs film. The volatile materials were then distilled off and the solid film was heated at 420°C for 18 hours. Some H₂ was produced at this temperature, and this was considered by Ring and Schlyer to demonstrate that there was homogeneous adsorption of an AsH₃ species, which had not completely decomposed to arsenic at the lower temperatures.

 CH_4 was also produced at 420°C and this was attributed to decomposition of the adduct species $(CH_3)_{3-x}GaAsH_{3-x}$ which had been formed at the lower temperatures. The amount of CH_4 produced was observed not to be related to the amount of CH_3 groups present, which led to the assumption that CH_4 elimination only occurred at the surface. The conclusion was that the partially decomposed adduct species at the surface hindered GaAs growth.

Ring and Schlyer [2.1] determined that the reactions at the surface were heterogeneous, where two mechanisms were considered. The first mechanism was the adsorption and subsequent reaction of both precursor species (Langmuir-Hinshelwood mechanism). The second mechanism was the adsorption of one precursor species, which would then react with the other precursor species in the gas phase (Eley-Rideal mechanism). Which particular mechanism was occurring was distinguished by the reaction orders with respect to AsH₃ and TMGa for the reaction:

$$(CH_3)_3Ga + AsH_3 \rightarrow (CH_3)_2GaAsH_2 + CH_4$$
(2.1)

The reaction order was determined by the change in AsH₃ consumption with respect to either AsH₃ partial pressure or TMGa partial pressure, while the pressure of the other precursor was kept constant. The reaction order for TMGa was less than one, leading Ring and Schlyer [2.1] to the conclusion that TMGa was adsorbed before reacting. However, the reaction order of AsH₃ was only a little less than one, but with experimental error it could not be concluded that adsorption occurred prior to reaction. It was thought that AsH₃ probably did adsorb before the first CH₄ elimination. The less than unity reaction order, which became more substantial with higher pressure, was thought to be due to either surface poisoning from atomic hydrogen and methyl groups, or to a reduction in the adsorption equilibrium constants.

2.1.1 In situ infrared spectroscopy monitoring of reaction products

In situ monitoring techniques have been used to try to determine what reaction mechanisms are occurring between TMGa and AsH₃. For example, infrared spectroscopy [2.3] has been used to measure samples in the gas phase over the substrate area. Species present in the hot zone were sampled using a capillary connected to a spectrometer and then directed back into the exhaust flow. The decomposition of TMGa and AsH₃ was measured by introducing three different precursor mixtures into the reactor chamber. The first was TMGa with the H₂ carrier, the second was AsH₃ and H₂,

and the final one was TMGa and AsH_3 with H_2 . This was to determine the characteristics of precursor decomposition.

In the first mixture, CH_4 was detected at 400°C, and above 580°C the amount detected was saturated. Decomposition of TMGa was observed to increase significantly between 500°C and 580°C, and was completely decomposed above 580°C. In the second mixture, the IR measurements showed the disappearance of AsH₃ between 650°C and 710°C, where decomposition was significant. Beyond 750°C, no more AsH₃ was detected due to complete decomposition. With both precursors in the mixture measurements showed increased decomposition from 400°C to 560°C, with CH₄ concentration increasing with temperature as TMGa and AsH₃ were consumed. IR measurements also detected a new absorption peak of an unknown material.

The molar flow of TMGa was kept constant, and the peak intensity of the unknown material at the new absorption peak was observed to increase with AsH₃ concentration (Beer-Lambert law). The TMGa supply was then stopped, and the new absorption peak disappeared to leave only AsH₃ detected. This led to the conclusion that the unknown material was also dependent on TMGa and that the material was composed of both precursors. It was proposed [2.3] that this material was an intermediate in the reaction.

The presence of TMGa was observed to affect the AsH₃ concentration, and it was concluded [2.3] that this was caused by one of two conditions. The first possibility was that decomposition was promoted due to GaAs formation in the vapour phase, with consumption of both Ga and As species. The second possibility was that formation of Ga or metalorganic radicals from TMGa decomposition reacted with AsH₃. GaAs wafers were placed within the reactor to measure the decomposition effects of the precursors. However, it was not possible to measure a difference in AsH₃ concentration compared to measurements carried out without wafers present.

Deposition of GaAs and Ga on the reactor walls was observed in the decomposition experiments. Due to the larger surface area of the wall relative to the wafer, it was

thought to be possible to measure the effect of GaAs and Ga on AsH_3 decomposition. AsH₃ with H₂ were introduced into the reactor at 530°C, and then TMGa was added for 6 minutes. As a result, the detected amount of AsH_3 decreased. Stopping the supply of TMGa, the detected AsH_3 concentration increased, but did not recover to the original level, due to the effect of deposited GaAs and Ga on the walls.

An estimation of the effect of GaAs and Ga in the reactor was implemented by introducing AsH_3 with H_2 at 530°C into a clean reactor. Following this, the AsH_3 was purged from the chamber with H_2 . TMGa was then introduced with H_2 at the same temperature and then the chamber was purged with H_2 . Adding AsH_3 with H_2 again resulted in a decreased concentration of AsH_3 . Following this procedure repeatedly and measuring the concentrations of detected AsH_3 resulted in an exponential decrease of AsH_3 with a corresponding increase in total input of TMGa. This proved that deposited GaAs or Ga on the reactor wall catalyzed AsH_3 decomposition [2.3].

Further study by Denbaars and co-workers [2.4] into the mechanism of GaAs deposition from TMGa and AsH₃ was carried out to develop an understanding of the growth process and to build on existing theories as described above. Decomposition of TMGa in a horizontal reactor with H₂ carrier gas flow of 1.25 cm s⁻¹ was analysed by infrared spectroscopy on species in the exhaust flow from the hot zone in the gas phase. No change of TMGa from the input concentration was observed at 380°C, but a decrease was observed from 400°C. At 460°C the gas concentration was measured to be zero, signifying complete decomposition at this temperature.

When GaAs wafers were placed inside the reactor hot zone, little difference was observed in the decomposition rate at these temperatures. The TMGa decomposition correlated with CH₄ evolution in this study [2.4]. CH₄ concentration was observed to increase until approximately 500°C, after which it saturated. Figure 2.1 shows a plot of the ratio of CH₄ present to the TMGa concentration loss at temperatures ranging from 350° C to 550° C. It gives an indication of the number of CH₃ groups dissociated from the TMGa molecule during its decomposition.



Figure 2.1: Ratio of CH₄ concentration to the change in concentration of TMGa, i.e. $R = [CH_4] / [\Delta TMGa]$ vs. temperature. The low temperature value of R is 2.0, while above 500°C, R = 3.3, after Denbaars *et al.* [2.4].

Below 460°C, the ratio of CH₄ to TMGa was observed to be 2, increasing to 3 above this temperature. At the lower temperatures, the results suggested decomposition of TMGa occurred by other pathways other than homogeneous decomposition. Monomethylgallium (MMGa) was considered likely to deposit onto the reactor walls, with all CH₃ groups dissociating in the gas phase above 465°C. It was concluded [2.4] from the evidence that release of the third CH3 group was insensitive to Ga and GaAs wall deposits and GaAs wafers at these higher temperatures. No CH₄ was detected from the wall deposits heated to 500°C when gaseous TMGa was absent. The loss of the final CH₃ group was determined to have high activation energy. This was due to the sharp transition between the temperatures where 2 or 3 CH₃ groups were lost from TMGa and this agrees with other investigations [2.1, 2.5].

The decomposition of AsH_3 in H_2 at the same flow rate was measured by infrared spectroscopy. The decomposition rate was observed to increase gradually, and on reaching a temperature of 650°C until all AsH_3 was consumed. The presence of GaAs wafers increased this decomposition rate significantly, and the presence of Ga and nonstoichiometric GaAs wall deposits enhanced AsH_3 consumption, as well as having TMGa present in the gas flow. From this study [2.4] the effect of TMGa in the gas

phase and the effect of Ga and GaAs wall deposits on surface reactions were not differentiated from each other.

The activation energy of AsH_3 in H_2 was measured as a first order reaction and found to be 34 kcal mol⁻¹. Below 530°C, the presence of GaAs surfaces lowered this activation energy to 18 kcal mol⁻¹, but above this temperature the value increased to that determined for homogeneous decomposition. It was determined that at temperatures above 530°C homogeneous decomposition of AsH_3 dominated. The presence of TMGa was not found to alter the activation energy substantially, but had significant effect on increasing the decomposition rate.

Spectroscopic infrared data from Leys and Veenvliet [2.6] demonstrated the consistent presence of AsH₃ in the gas phase. This was concluded to show that AsH₃ decomposition only occurred at the surface, but could also demonstrate AsH₃ regeneration. The study also concluded that the model showed that an increase in p_{AsH_3} did not increase surface coverage of AsH(s) and As(s) because they were generated from AsH₂. The rate of AsH₂ production was controlled by the 'CH₃ production rate. The reaction rate of AsH₃ with 'CH₃ radicals increased in the model with increasing p_{AsH_3} . However, this was found to reduce reaction of AsH₃ with H[•] radicals as less 'CH₃ radicals were present in the system to react with H₂ to produce H[•] radicals.

With greater p_{TMGa} , the surface coverage of MMGa(s), AsH(s) and As(s) has been observed to increase [2.7]. The surface coverage of the As-species increased with concentration of 'CH₃ radicals, agreeing with Reep and Ghandi [2.5]. The gas flow dynamics was considered important in the model [2.7] where increased gas velocity reduced the residence time of the reacting species leading to less gas phase decomposition and more kinetic control. A small gas velocity increased mass transport dependence on the growth rate where greater residence times of the species allowed more opportunity for diffusion of the species to the substrate surface. Reactor configuration was therefore considered to be very important.

2.1.2 In situ mass spectroscopy to monitor reaction products

In a further study by Nishizawa and Kurabayashi [2.8], mass spectrometry was used in conjunction with infrared spectroscopy. An attempt was made to identify the peak at 2080 cm⁻¹ in IR spectra [2.3] from the reaction between TMGa and AsH₃ in the temperature range 450 - 520°C. Species that were proposed to have been detected from molecular mass results included AsCH₃ (90), AsH₂CH₃ (92), AsH(CH₃)₂ (106) and As(CH₃)₃ (120). The peak at 2080 cm⁻¹ from IR spectra was suggested to correspond to AsH(CH₃)₂ or AsH₂CH₃ due to the As-H vibration frequency in AsH₃ (2122 cm⁻¹) being close to this peak.

The decomposition of AsH_3 was enhanced by the presence of TMGa and Ga wall deposits. TMGa was initially introduced with H_2 into a clean reactor and Ga was deposited onto the reactor wall. The enhancement of AsH_3 decomposition was measured as a function of TMGa injection time, and found to increase when TMGa was supplied for longer periods of time. Varying the AsH_3 injection time made no difference to the decomposition rate. Increased AsH_3 decomposition was determined [2.8] to be due to the quantity of Ga and GaAs on the wall. The wall deposit changed into polycrystalline GaAs after AsH_3 injection.

In Figure 2.2 GaAs can be seen to be more effective than Ga at catalyzing AsH_3 decomposition. AsH₃ decomposition is seen to be greatest on the Ga(111) surface. The deviation of D from D₀ was determined to correspond to the reaction rate on each surface, where D = log (I₀ / I), with I₀ = transmission without AsH₃ and I = transmission of AsH₃ with the sample. It was proposed by Nishizawa ansd Kurabayashi that decomposed AsH_x species adsorbed on to the substrate surface and then evaporated from the surface and deposited downstream from the inlet. A gallium (Ga) melt was deposited in the reactor by the pyrolitic decomposition of TMGa above 600°C without the presence of H₂. With this Ga melt present, polycrystalline GaAs was deposited slowly with the supply of AsH₃, which increased in rate after a period of time. A film deposited on the wall near the Ga substrate region and was expected to be GaAs. It was

thought that Ga or GaAs was deposited on the wall from the Ga melt by being transported through the vapour phase, occurring only when AsH_3 was supplied into the reactor.

Figure 2.2 has two curves representing the reactor with a Ga melt with floating polycrystalline GaAs on it and polycrystalline GaAs on the wall ($\mathbf{\nabla}$). It also has a curve representing the reactor with only a Ga melt with floating polycrystalline GaAs on it ($\mathbf{\nabla}$). The enhancement of AsH₃ decomposition was determined to be due to reaction with Ga initially, and then by reaction with GaAs on the reactor wall. A silicon (Si) wafer was placed downstream from the Ga melt facing it at a distance of 1 cm. When only H₂ was introduced into the reactor at 600°C for 1 hour, no deposition was observed on the Si surface, but when AsH₃ was introduced deposition did occur.



Figure 2.2: Temperature dependence of the enhancement of AsH₃ decomposition, after Nishizawa and Kurabayashi [2.8].

Auger spectra determined the deposit on the Si substrate to be GaAs from the ratio of the Auger signal intensity between Ga and As. It was proposed [2.8] that GaAs was formed from the reaction of AsH_3 with the Ga melt, and deposited downstream of the Ga melt.

The experiments were carried out at a temperature of 600°C, which is in the diffusionlimited growth regime where mass transport limits the growth rate.

2.1.3 Existing investigations into the reaction mechanism for GaAs deposition

Reep and Ghandi [2.5] studied GaAs growth over a wide range of temperatures. The investigation was into the effect of different temperatures and of substrate orientation in epitaxial growth. They observed there to be 3 distinct growth regimes (Figure 2.3). Low temperature growth (<600°C) showed rate dependence on surface reactions, mid temperature growth (600°C< x <850°C) depended on mass transport of reacting species to the substrate surface and the high temperature process (>850°C) was dependent on desorption of the adsorbed species.



Figure 2.3: Growth rate as a function of temperature, taken from Tischler [2.9].

At 500°C, the partial pressure of TMGa (p_{TMGa}) was varied while p_{AsH_3} was kept constant. The same was done varying p_{AsH_3} while keeping p_{TMGa} constant. The substrate crystal orientations used in the investigation were (100), (110), (111)As and (111)Ga.

The first 3 orientations showed a slight sub-linear variation of growth rate with p_{TMGa} and a weak dependence on p_{AsH_3} . With the (111)Ga orientation, the growth rate was non-linear with p_{TMGa} and had a significant dependence on p_{AsH_3} . The Langmuir-Hinshelwood mechanism was the proposed process for low temperature deposition. This was because the growth rate was sub-linear with respect to both TMGa and AsH₃ for all orientations. It was thought [2.5] that arsenic adsorption dominated on the (111)Ga orientation.

This postulation was supported by the measured activation energy of 92.0 kJ mol⁻¹ at the (111)Ga surface for the deposition of GaAs. This was close to the activation energy measured for AsH₃ decomposition of 97.1 kJ mol⁻¹ producing AsH₂. The measured activation energy on the (111)As face was lower, which led to the conclusion that the Ga species enhanced the probability of chemisorption of AsH₂. This was attributed to coordination between the two species, and agreed with the investigations reported above [2.1, 2.3]. The decomposition would then be limited by the partial pressure of TMGa because it is typically the minority species. This was confirmed by experimental results (Figure 2.4).



Figure 2.4: Growth rate vs. partial pressure of TMGa for GaAs epitaxial layers at constant $p_{AsH_3} = 3.3 \times 10^{-3}$ atm and 500°C, after Reep and Ghandi [2.5].

It was proposed [2.5] that both precursors adsorbed at the surface even at low temperatures, but homogeneous decomposition of AsH_3 could not occur to any significant extent. Evaluation of the dissociation energy of the final CH_3 group from Ga (324.3 kJ mol⁻¹) and the observed activation energy for GaAs deposition indicated that at the low temperature range, the adsorbed Ga species was likely to be GaCH₃ (MMGa). Decomposition of TMGa would be limited by dissociation of this last CH_3 group. For AsH₃, it was proposed [2.10] that the dissociation of the first H atom or the energy required for adsorption on to the surface would be the rate limiter for decomposition.

Decomposition of TMGa to Ga had not been observed below 800°C [2.11] when no As species was present. MMGa and AsH were concluded by Reep and Ghandi [2.5] to be the most probable species at the surface at low temperatures. With an abundance of H_2 (carrier gas), it was expected that there would be a large surface population of adsorbed AsH(s). This would promote dissociation of the arsenic dimer (As₂) and arsenic tetra (As₄) species. Thus at temperatures above 420°C, the study suggested [2.5] that it would be unlikely that the adduct (CH₃)_{3-x}GaAsH_{3-y} would sequentially decompose at the surface, with removal of CH₄.

Alternatively, it was reported that MMGa could adsorb and then diffuse along the surface to a Ga kink site, where it may then react with adsorbed AsH(s) or As(s) to form GaAs. The over-pressure of AsH₃ typically used suggested that reaction between the Ga- and As-containing species might occur faster than the Ga-species would diffuse to the Ga kink site. It was suggested that both precursor species could diffuse to their appropriated kink sites before decomposition, or that they could interact to form the mobile adduct (CH₃)GaAsH, which would diffuse to a growing crystal step (Figure 1.1, page 3).

A later study [2.12] concentrated on GaAs epitaxial growth over a pressure range between 0.1 and 1 atmosphere. Reep and Ghandi [2.5] also varied temperatures over the range of the different growth regimes established. At low temperature, the growth rate was found to increase with temperature. The growth rate was measured as a function of

pressure and gas velocity at varying temperatures. A pressure of 1 atm with gas velocity of 1.9 cm s⁻¹, 0.1 atm and 5.8 cm s⁻¹, and 0.1 atm and 1.9 cm s⁻¹ were used. At the latter condition, the growth rate was observed to decrease with increasing temperature in the diffusion-limited temperature range due to greater wall deposition upstream of the susceptor. This was suppressed when increasing the velocity to 5.8 cm s⁻¹ at this pressure range. The effect was not so pronounced at the lower temperatures thus agreeing with the assumption [2.5] that the process is kinetically limited at low temperatures and limited by diffusion / mass transfer at intermediate temperatures.

The growth rate was observed by Heinecke *et al.* [2.12] to be non-dependent on AsH_3 pressure. A dependence on TMGa pressure was noticeable, thus agreeing with Reep and Ghandi [2.5]. Saturation of the rate occurred at TMGa pressures much lower than the AsH_3 pressure. The rate increased with gas velocity until it saturated, but it was suspected that an increase in gas velocity would have a cooling effect. Limitation of the rate was proposed [2.12] to be due to blocking of the surface by adsorbed species. It was thought unlikely that species from TMGa would be blocking the sites. It was expected that saturation of the rate would be observed at a given temperature, rather than due to change in gas velocity or system pressure.

The observed non-dependence of growth rate on AsH_3 pressure in this study ruled out blocking by As-species. However, Reep and Ghandi [2.5] observed a weak dependence on AsH_3 pressure for all orientations, except for the (111)Ga face where there was a strong dependence. It was also proposed [2.12] that hydrocarbon species could be blocking the site on the surface. Injection of CH_4 into the system was found to reduce the reaction rate giving evidence for this argument.

2.2 Existing MOVPE investigations in process reactors

Since Manansevit first used organometallics in VPE, research has been carried out attempting to model growth, particularly of GaAs using trimethylgallium (TMGa) and arsine (AsH₃) as precursors. At process temperatures surface reactions are generally fast and growth is limited by diffusion of the gas species to the substrate surface. Therefore, there have been many investigations into gas flow patterns with mathematical representation of mass transfer of reacting species in the gas phase. This section also briefly looks at other processes in the industry and discusses the effect of reactor configuration.

2.2.1 Importance of reactor design

The design of the reactor is important because it has significant influence on the uniformity of deposition and the capability of forming abrupt interfaces. The design of MOVPE reactors involves a cold wall tube, cooled by air or water, usually made from quartz, with a heated zone for deposition to occur [2.13]. Manasevit [2.14] carried out his investigation in a vertical reactor tube with the gas inlet at the top. Other designs are also used today that have been developed by various manufacturers. Figure 2.5 [2.13] displays some reactor designs that are available commercially for metal-organic chemical vapour deposition (MOCVD) processes. The leading companies that manufacture MOCVD reactors are:

- Veeco, who produce vertical reactors,
- Aixtron, who manufacture horizontal reactors,
- Thomas Swan who produce both types.



Figure 2.5: (a) Vertical reactor, (b) horizontal reactor with rotating susceptor, (c) horizontal reactor with tilted susceptor, after Leys [2.13].

A gas flow with a velocity of approximately 30 cm s⁻¹ through the reactor tube, and a single hot zone are typically used in MOVPE experiments. Knowledge of the behaviour of the carrier gas allows the evaluation of how well different designs operate. There are two types of fluid transport within the reactor. Firstly, there is forced convection from the flow of the carrier gas through the reactor, resulting from the pressure difference between inlet and exhaust. The second type of fluid movement is free convection. This is caused by varying temperature within different regions in the system. When a gas

with low thermal conductivity and high fluid density is used, such as nitrogen (N_2) or argon (Ar), the flow pattern through the reactor is strongly influenced by free convection. This is not the case for less dense gases such as hydrogen (H_2) or helium (He).

Behaviour of the carrier gas depends on a number of factors, such as sudden expansions or restrictions in the reactor tube. Also the reactor pressure is of importance, reducing the pressure tends to smooth the streamline pattern to an ideal, laminar type flow [2.13]. A lower pressure operation reduces the residence time of the reacting gas mixture within the reactor chamber, and thus decreases the parasitic side reactions between the group III and group V compounds. The other advantage is the suppression of vortices in the gas flow by reduction of the mass of the gas, so reducing buoyancy and inertial forces. The reduction of vortices may be more significant in models for industrial processes [2.15]. High carrier gas flow rate and reduced reactor pressures allows freedom of convective instability. However, this makes the process more complex and costly when scaling-up for manufacturing.

In some reactor designs there is a tendency towards a decrease in layer thickness towards the downstream part of the reactor. This is due to depletion of the precursors in the gas phase. Tilting of the susceptor slightly so that the reactor cross-section is reduced increases the gas velocity along the length of the reactor minimizing this effect (Figure 2.5c). Rotation of the susceptor is another design to optimize thickness homogeneity (Figure 2.5b). For manufacturing scale the reactors are multiwafer designs to gain more production throughput [2.13].

2.2.2 Large scale manufacturing in MOVPE

The MOVPE growth process has improved with the use of multiwafer reactors, such as the planetary reactor manufactured by Aixtron, which was introduced in 1988 and has been successful in the growth of a variety of structures. A number of parameters need to be controlled to give experimental optimisation, which can be time consuming.

Theoretical studies based on numerical simulations have aided the design and application of the reactor [2.16]. Group III metal-organics and group V hydrides, both diluted in the H_2 carrier gas, are introduced through separate inlet channels at the centre of the reactor and flow in a radial direction outwards along the growing layers. The reactor top is cooled by a mixture of Ar or N_2 and H_2 , allowing control over the ceiling temperature through the gas composition [2.17]. Figure 2.6 is a schematic example of the cross-section of an Aixtron multiwafer reactor.



Figure 2.6: Schematic of the Aixtron multiwafer planetary reactor, after Bergunde and co-workers [2.16].

MOVPE has been the growth technique of choice for larger scale manufacturing of compound semiconductor devices, mainly because of the lower product costs and the ability to grow complex structures. For large scale production the thickness composition and doping of each layer of the grown device structure must fall into a specified range. The variation within each wafer, from one wafer to the next, and after a number of runs must be small enough to give an acceptable yield after full device fabrication. In the manufacturing industry, reproducibility is as important as uniformity, this is achieved by frequent calibration and a tight control on parameters. Factors such as metal-organic bubbler level and temperature, mass flow, pressure drift and wafer temperature affect the growth rate, composition and doping level.
The number of calibration runs and frequent measurements on test structures has an adverse impact on the equipment throughput and product cost. Equipment throughput and product cost has the potential to improve with the use of *in situ* real-time control of the growth rate and composition. The throughput of a system (wafers/year) is the number of runs carried out in a year, multiplied by the number of wafers per run (capacity). The true throughput of a system is reduced by equipment downtime for maintenance, cleaning, source changes, the need for calibration or test runs, and failures of the system components or facilities. By running the system continuously over a sufficient time all maintenance operations and typical failures can be observed.

For example, in a multiple wafer rotating disc reactor, the lowest cost results from using the highest capacity reactor, as long as it is fully utilised. Under-utilising a larger system increases the product cost. Automation of the loading process can be achieved with a removable wafer carrier in the reactor design, and wafer handling can be done off-line increasing the system throughput [2.18]. The design of the planetary multiwafer reactor has changed over the years with reactor models up-scaled in size to include more and larger wafers per reactor. The need to control and optimize the growth process for production of highly sophisticated semiconductor and optoelectronic devices led to research in modelling the deposition process.

Bergunde *et al.* [2.16] found differences between published results and their experimental findings. This led them to model flow, heat transfer and multi-component mass transfer with homogeneous and heterogeneous reactions of predominant species in a commercial radial flow horizontal multiwafer planetary reactor. This was an effort to optimize the growth process. Their theoretical studies included investigations into the effects of different growth parameters on layer thickness profiles and also on parasitic deposition on the reactor walls. They found that gas phase species were depleted downstream from the inlet, determined to be caused by parasitic growth on the quartz walls of the reactor. The results of the parasitic growth showed that different quartz top plate temperatures of the Aixtron planetary reactor resulted in different types of parasitic

deposit. An optimum temperature for minimal parasitic growth was achieved, but it still occurred nonetheless.

2.2.3 Time dependent model of mass transfer of gas phase species

Mountziaris and co-workers [2.19] developed a two-dimensional, time dependent model of mass transfer along the vertical mid-plane of the reactor to describe mass transfer by convection, diffusion and thermal diffusion. Gas phase and surface reactions were initially neglected. The investigation was directed towards measuring the duration of gas phase precursor concentration adjacent to the substrate, before it changed from one steady state to another. This was important when considering the production of heterostructures where interface abruptness is important for device operation. The TMGa precursor concentration was investigated in a filling experiment, because the diffusion of this species is the limiting factor for process conditions.

The time required for the TMGa precursor in the gas phase adjacent to the substrate to reach a new steady state was defined as t_{sub} and the temperature of the substrate as T_s . The effect of different flow velocities on t_{sub} was studied. At low velocities (5 cm s⁻¹), t_{sub} was observed to be high due to the roll effect [2.20, 2.21], which delayed the establishment of the new steady state. At higher velocities (7 cm s⁻¹), t_{sub} fell significantly because the increased flow eliminated the roll effect downstream and reduced the upstream free convection. At 10 cm s⁻¹, t_{sub} was observed to change only very slightly, further increasing the velocity beyond this value did not affect the interface abruptness. However, it did reduce reactant conversion due to the decrease in residence times. At 10 cm s⁻¹, the spiralling effect due to free convection was eliminated for all values of T_s . The height of the reactor may influence the effect of free convection.

Horizontal reactors of height 5 cm, 3 cm and 1 cm were used in simulations. It was found that a reactor with small height did not allow the heated gas to expand freely in the vertical direction, but longitudinally instead. Thus, the horizontal velocity was

increased locally, t_{sub} decreasing with reduction in height. One effect of the gas phase reactants at process temperatures considered transport of lighter precursor fragments to the substrate surface. Fragment species will have higher diffusivity and lower thermal diffusivity than the parent species. When Ga was considered instead of TMGa, t_{sub} was found to reduce. A hypothetical precursor ten times the diffusivity of TMGa was considered, t_{sub} was found to be approximately 1 s greater than that of TMGa. The conclusion was that t_{sub} was controlled by forced convection (horizontal direction) and that gas phase reactions have no effect on t_{sub} . It was believed, however, that the growth rate would change due to the dependence of the growth rate on the diffusivity of the precursor, when process conditions were employed.

Simulations were also carried out at pressures ranging from 0.1 to 1 atm, with constant mass flow rate. Values of t_{sub} were observed to decrease mainly due to the amplified gas velocity, but not significantly, because at critical increased velocity values of t_{sub} were observed to converge. The length of the substrate area L_s and entrance L_e were used in simulations also. The effect of increasing L_s did not make much difference to t_{sub} because the larger substrate area was counteracted by the expansion of gas due to heating. Enlarging L_e increased t_{sub} because the precursors were less concentrated at the substrate surface and substrate coverage took longer.

Surface reactions were also considered, the effect of two precursors with the properties of TMGa and AsH₃ was investigated. The surface reactions were simplified to three reactions: adsorption of species 1, adsorption of species 2, and reaction of the two adsorbed species at the surface to form GaAs. Selected chemisorption of Ga on As, and As on Ga was assumed. The V/III ratio used was 10, with $T_s = 750$ K (477°C) and $T_s = 900$ K (627°C). Growth is limited by surface kinetics at the lower temperature and limited by gas phase diffusion at the higher temperature. The value of t_{sub} was found not to deviate much from the original model. It was recognised [2.19] that experimentally, the growth rate at the initial stages of heteroepitaxy could be significantly lower than the steady state value. This was because of nucleation effects, which would require *in situ* monitoring during film growth.

2.2.4 Gas flow patterns

The gas flow pattern in a horizontal quartz tube was analysed in 1972 by Koga and Sugawara [2.20]. This was done using titanium dioxide (TiO₂) particles which were traced by a camera photographing the flow patterns at the end of the tube. TiO₂ particles were formed by mixing titanium tetrachloride (TiCl₄) vapour with the flowing gas from a capillary tube connecting a TiCl₄ source to the quartz tube inlet. Reaction with moisture in the carrier gas formed the TiO₂ particles. Both rectangular and circular quartz tubes were used, with He and N₂ as carrier gases, He being similar in fluid characteristics to H₂ which is commonly used in MOVPE. Gas flow rates were varied from 0 to 60 L min⁻¹ with the pressure ranging from 160 to 760 Torr. An iron plate was placed on silicon carbide heaters at the bottom of the tube to obtain uniform temperature distribution.

At a small flow rate, the flow pattern of the gas moved upward from the centre of the plate and down along the tube wall. The distribution of temperature was found to be highest at the centre of the tube and decreased toward the walls. This was found to be independent of tube geometry. At higher flow rates, the vortex patterns were shifted to the corners of the tube cross section for He, where the gas velocity was possibly smaller than at the centre of the tube giving rise to free convection effects.

Further work on gas flow effects were investigated in 1986 by Moffat and Jensen [2.21] and also by Giling and co-workers [2.22]. Both research groups studied the growth of GaAs from TMGa and AsH₃ and modelled their work based on diffusion of the reacting species. Jensen and Moffat [2.21] used a model employing TMGa as the only diffusing species, with a fast surface reaction. It was widely accepted at this time that mass transfer of the Ga species controlled GaAs growth, but there was limited understanding of the decomposition of TMGa. Velocities at the surface were assumed to be zero for simplicity, which was conventional due to the dilute concentrations of reactants used in MOVPE. Model predictions were developed for a rectangular horizontal reactor with adiabatic side walls and another with water cooled walls with ceiling temperature of 300

K (27°C). The susceptor temperature was 1000 K (727°C) in both cases with a H_2 carrier gas.

For the reactor with side walls at constant temperature, the model predicted the expansion and rise of the gas over the hot susceptor. Then at the corners it would roll due to a density difference between the gas moving at the sides and travelling in the middle, which was flowing faster and therefore less heated due to the larger velocity. With H_2 , the density gradient disappeared and the rolls ceased. For reactors with larger height, or with greater differences between ceiling and susceptor, or with a denser gas such as N_2 , the rolls sometimes persisted even when the flow has established.

The flow patterns influenced the deposition profiles on the substrate. The roll pattern of the gas depleted the precursors over the substrate. Then the flow stabilized and the gas could flow downwards over the substrate and increase the deposition rate in the mid section. Film thickness variations were observed [2.21] to occur across the substrate. The reactor with water cooled side walls was predicted to make the gas denser at the walls rather than at the reactor centre, giving a spiral effect in the flowing gas. The density gradient was found not to diminish as the flow developed, leading to the presence of film thickness variation all the time.

2.2.5 Factors affecting the growth rate

Giling and co-workers [2.22] used numerical simulation of process parameters and compared their findings to experimental data. A simplified model was used to describe temperature distribution and velocity profiles. These influence the concentration profiles of the reacting species resulting from mass transport to the substrate, and chemical reactions. Flow instabilities were observed to affect the growth rate distribution over the substrate as Moffat and Jensen observed [2.21]. Experiments were carried out in rectangular reactors, as opposed to cylindrical designs, due to the existence of lateral temperature variations in cylindrical tubes which was found to influence growth rates.

The model considered growth rates which were calculated from concentration profiles within the reactor. Growth was assumed to be limited by diffusion of the reacting species with forced convection dominating the gas flow, neglecting mixing due to free convection. Experiments were carried out [2.22] using a heated susceptor fixed at 700°C. In most cases, the ceiling was cooled by water and the side walls by air. An arsenic film was observed during MOCVD, which reflected heat, changing the temperature at the susceptor significantly after a period of time.

Giling and co-workers adapted the reactor by depositing a metallic silver mirror to the bottom of the water cooler placed on top of the reactor ceiling. This removed the problem of varying wall temperature. The growth rate was found to be independent of temperature and partial pressure of AsH_3 within a wide range of V/III ratio, but there was a linear dependence on the partial pressure of TMGa. This was found to be the case when using H_2 or N_2 as the carrier gas, concluding that diffusion of the gallium precursor limited the growth rate of GaAs.

TMGa in H_2 was reported [2.22] to decompose rapidly at 420°C and was expected to only deposit in the lower region of the reactor because the water cooling of the ceiling was expected to prevent deposition at the ceiling. In H_2 , liquid gallium formed on the quartz susceptor and GaAs substrate, while in N_2 , gallium droplets were only observed on the GaAs substrate. A polymeric film would deposit onto the susceptor. This suggested that the GaAs substrate acted as a catalyst for the decomposition of methylgallium species, which led to the conclusion that TMGa in general does not fully decompose in either H_2 or N_2 . Growth rates were measured at different positions along the reactor. Downstream, towards the exhaust, the growth rate was found to have no difference when the GaAs substrate was present or not. It was determined by Giling and co-workers [2.22] that the decomposition rate of TMGa was equal at all positions on the hot susceptor and independent of the presence of a GaAs substrate.

The growth rate was seen to decrease along the susceptor and gas phase depletion considered to be the likely cause. The deposition rate was observed to decay

exponentially. This occurred more rapidly in H_2 than in N_2 due the diffusion coefficient of the reacting species being much higher in H_2 than in N_2 . In reactors which were air cooled, the growth rates were observed to decay quicker than in the water cooled reactors. This resulted in the conclusion that TMGa decomposition occurred at the upper wall of the reactor as well as at the substrate. It was reported [2.22] that TMGa decomposition begins to be significant above 400°C and is complete at 460°C. The temperature was measured to be 700 K (427°C) at the upper wall of the reactor in a developed flow region downstream. The growth rate decay was measured to be more rapid at further downstream axial positions of the reactor. This confirmed the theory of Giling and co-workers that complete TMGa decomposition only occurs at the hot surface and not in the gas phase.

In reactors which were greater in height, vortices were expected to form due to free convection. At higher flows, growth rates upstream (closer to the inlet) became constant. When using H_2 as carrier gas, growth rates measured [2.22] downstream at the mid plane of the reactor were smaller than at the sides, which was the opposite for N_2 . This can be explained by the presence of vortices described earlier from the gas flow investigations of Moffat and Jensen [2.21].

Bergunde *et al.* [2.23] investigated the effect of the gas flow and the relative concentration (ratio) of the precursors. The gas flow velocity decreased as the gas travelled through the horizontal reactor and over the wafer. The flow pattern and rate profile altered when the total flow was kept constant and only the ratio of precursor flow was changed. Experimentally, the growth rate profile shifted downstream into the wafer with decreasing ratio. On a rotating wafer the film had a concave profile with a decrease in ratio, as in Figure 2.7.



Figure 2.7: Diagram to show a concave growth thickness profile, after Bergunde and co-workers [2.23].

A change in the V/III ratio affected the flow velocity of the AsH_3 precursor, at high ratio the AsH_3/H_2 mixture moved more slowly and was dense relative to a low ratio, which led to faster arsine decomposition. Flow and ratio affected the position of maximum growth and the downstream depletion slope of the rate profile. It was observed that for a homogeneous thickness distribution the maximum needed to lie outside of the wafer, averaging with rotation of the wafer. A shift upstream of the rate profile was observed, with an increase in the pressure, due to a faster decay of the precursors towards the outlet. The higher pressures led to greater gas phase depletion, lower pressures being preferable for obtaining homogeneous growth.

Dauelsberg *et al.* [2.24] modelled gas phase transport based on the solution of the coupled flow, heat transfer and mass transport equations. The growth rate distribution on the susceptor was directly affected by temperature changes in the reactor. A hotter reactor environment at low cooling rates enhanced diffusive transport and slightly increased the growth rate upstream. Hydrogen content below 40% in the cooling gas caused a decrease in the growth rate downstream. This caused the wall and ceiling temperature to be hotter relative to when hydrogen content was more than 40% of the cooling gas due to the good heat conductivity of hydrogen. The overall effect on a rotating wafer was that the film had a convex thickness profile, as in Figure 2.8.



Figure 2.8: Diagram to show a convex growth thickness profile, after Bergunde et al. [2.24].

The growth rate profile on a static wafer was directly affected by three different influences:-

- 1) The temperature in the inlet region and the resulting losses upstream,
- 2) The temperature in the middle of the reactor,
- 3) Possible ceiling deposits affecting the growth downstream [2.24].

The diffusion coefficient was strongly dependent on temperature. For a constant mass flow, the thermal distribution and heat transport in the reactor were almost insensitive to pressure. This was because the heat convection was proportional to mass flow, and the thermal conductivity coefficient and gas viscosity were virtually independent of pressure. The mass transport velocity was considered due to its increase with a reduction in pressure [2.15]. For typical conditions in MOVPE, released heat from reactions of the relatively small amounts of active components in the input flow are insignificant. Radiation is the predominant mode of heat transfer, as temperatures for the growth of conventional III/V compounds are around 650-750°C.

The reactor enclosure was considered [2.17] in a further study, with semi-transparent spectrally dependent radiating walls, with carrier gas inside and ambient outside of the reactor chamber. Heat transfer from surfaces facing the wall and conduction through the carrier gas were thought to contribute to the energy flux to the internal side of the wall. Energy was lost from the wall to the ambient by radiation and cooling by the surrounding (ambient) gas. Diffusion of species determined the growth rate with mass transport-limited growth on the substrates. For kinetically-limited deposition on the quartz walls, the net mass fluxes were balanced with a surface reaction rate for formation of the solid. The formed deposits were found to influence the wall temperature by increasing the inward reflectance at the solid-gas boundary, having severe impact on the process stability and reproducibility.

During the initial stages of GaAs growth, the wall temperatures rose by roughly 10°C with the formation of layers of a few hundred nanometres. Under non-optimized conditions, deposits at the inlet region gave rise to a change in the shape of the growth rate profiles on the upstream wafer edge. This affected reproducibility of growth rate and uniformity. Minimisation of material losses at the inlet region was achieved [2.17] by reducing the heating power locally.

Kadinski *et al.* [2.25] developed a mathematical model for numerical calculation of radiative heat transfer in MOVPE reactors in the mid-90s. It was found that

decomposition rates and saturated vapour pressure of the reacting species depended exponentially on the wall temperature. Therefore, comprehensive heat transfer calculations were needed to optimize the process. Deposition on the reactor walls added to the reflection effects inside the reactor changing the radiative properties. When specular walls are heated or coated by a film, the emittance, reflectance and transmittance properties will change. If a wall was coated with an As-deposit, it became opaque with a high emission coefficient. If it was polycrystalline GaAs deposited on the wall, two different values for emittance were obtained. One was for radiation directed into the reactor E_1 and the other was directed outside of the reactor E_2 .

In the case of GaAs deposited on the quartz wall, which has high reflectivity, $E_1 < E_2$, the radiative exchange between the susceptor and wall diminished leading to a temperature decrease at the wall. However, additional absorption and irradiation of the GaAs film also caused a rise in the wall temperature. There were therefore two effects acting against one another, the dominant effect depending upon the film optical thickness τ_f . A thin GaAs deposit was expected to be diffusive with high reflectivity and an optical thickness close to zero, cooling the reactor wall. A relatively thick deposit had a larger optical thickness and increased the wall temperature by absorbing radiation from the susceptor. An As-film was opaque and had a high emission coefficient, leading to an increase in wall temperature. GaAs substrates and polycrystalline GaAs deposits on the susceptor were found to decrease the susceptor emissivity leading to the decrease of the wall temperature. It was realised by Giling *et al.* [2.22] that the wall deposits and the effects of substrate and susceptor deposits needed to be taken account of when optimizing the MOCVD process, ideally preventing parasitic deposition [2.25].

2.2.6 Relative effects of parasitic growth and reactor temperature distribution

A decrease in temperature on the quartz wall was observed due to the presence of a deposit and found to increase the deposition rate of parasitic arsenic by more than one order of magnitude. Further work by Kadinski *et al.* [2.26] demonstrated the

39

dependence of interference phenomena on wavelength. Therefore they developed a more complex model for radiative heat transport. For simplicity it was assumed that wall deposits of GaAs and As were uniform. The GaAs deposit was assumed to be only present above the susceptor on the upper part of the wall because it deposited at warmer temperatures. The As-deposit was assumed to be deposited on the whole of the upper wall because it deposited at cooler temperatures. The graphite susceptor changed in emissivity as polycrystalline GaAs was deposited on it. The emissivity of the susceptor was expected to change from that of pure graphite to that of pure GaAs. It was found that the variation of the susceptor emissivity resulted in significantly lower wall temperatures.

The upper wall temperature was simulated by Kadinski *et al.* [2.25] during GaAs MOVPE in a horizontal reactor AIX 200/4 over a period of time. The results determined the temperature to vary with time. Temperature distribution on the ceiling for different film thicknesses on the wall and for different emissivities of the susceptor can be seen in Figure 2.9. The GaAs film deposit had an abrupt boundary as it only deposited at maximum wall temperatures, which can be seen where there is a step effect in the curve. The lowering of the temperature of the wall decreased the deposition rate of the polycrystalline GaAs. This temperature was significantly lower than typical process temperatures at the substrate. Thus deposition was limited by the kinetics at the wall instead mass transport of the reacting species. The interference effects induced by the wall deposit reduced further deposition there. The combined effect of this and that of the GaAs layer deposited on the susceptor can suppress parasitic growth of GaAs on the wall and result in stationary growth conditions at the wall after a period of time.



Figure 2.9: Temperature distribution along the upper walls of the reactor for different values of the GaAs deposit thickness and the susceptor emissivity. (1)-(3) Emissivity = 0.9, (4)-(6) emissivity = 0.5: (1) thickness 0 nm, (2) 400 nm, (3) 700 nm, (5) 400 nm, (6) 700 nm, after Durst *et al.* [2.26].

Parasitic As deposited on the wall had a large cooling effect of the wall temperature. The As-film had large reflectivity, reducing the radiative heat transport toward the wall compared to a pure quartz surface. Figure 2.10 shows cases with a deposit-free, and GaAs covered graphite susceptor [2.26].



Figure 2.10: Effect of the As film on the upper wall temperature distribution. (1), (3) Susceptor emissivity 0.9; (2), (4) 0.5. Solid line; pure quartz wall; dashed line; reactor wall covered by an As film, after Durst *et al.* [2.26].

A mathematical model based on flow and deposition of GaAs in a planetary reactor, manufactured by Aixtron, was developed by Bergunde *et al.* [2.23]. It confirmed that

under typical process conditions, mass transport of Ga species in the reactor determined The model accounted for homogenous chemical reaction of the growth rate. decomposition of trimethylgallium (TMGa) to monomethylgallium (MMGa). Mass transport was assumed to be decoupled from the flow and heat transfer to simplify calculations, considering dilute mixtures of precursors in the carrier gas. In the planetary reactor (Figure 2.6, page 29) the different densities of the gas mixtures, which were supplied through separate inlets, was observed to make the local gas density dependent on the concentration of the species. When calculating mass transport of Group III and Group V species, the flow and heat transfer within the reactor were taken into consideration. The distribution of the temperature on the ceiling was non-uniform and affected the deposition process significantly. The temperature profile in the reactor was evaluated and two extreme cases for the ceiling temperature were modelled. The first regime used H₂ as the heat conductivity gas on the top plate of the reactor, which is effective for heat transfer through the ceiling. The second regime used Ar as the heat conductivity gas on the top plate, using the same growth conditions as in the first regime, the ceiling being relatively hotter.

The different heat flows through the ceiling in the first regime led to high temperature gradients, established quickly compared to the hotter ceiling, causing a difference in the decomposition of TMGa between both regimes. For the colder ceiling, homogeneous decomposition of TMGa generating MMGa proceeded slowly. Significant amounts of TMGa were still present above the substrate. With the hotter temperatures at the ceiling, complete decomposition of TMGa occurred before it reached the middle region of the substrate. Polycrystalline GaAs was deposited on the hot parts of ceiling, shown in Figure 2.11. This led to a change in the temperature profile with time and was unsuitable to obtain reproducible results. The deposition of the heat conduction gas mixture can be altered to change the ceiling temperature. With increasing H_2 content the temperature decreased and the rate of parasitic deposition was reduced. The ceiling became too cold with too much H_2 content and arsenic condensed on the ceiling.



Figure 2.11: Thickness profile of polycrystalline GaAs deposition on the reactor ceiling measured and calculated for different compositions of Ar/H_2 cooling gas, after Bergunde and co-workers [2.23].

With high temperature profiles, thermal decomposition of TMGa was observed by Bergunde *et al.* [2.23] on the upper part of the inlet nozzle. Making this part slimmer and further from the susceptor decreased the temperature and significantly reduced the TMGa decomposition. A chemical model was produced by Bergunde and co-workers [2.23] consisting of multi-component mass transport equations for the gas phase components including decomposition reactions of the metal-organic precursor. They predicted temperature distribution in the reactor using heat transfer calculations. This assumed heat transfer through a medium not involved in any participating reactions with semitransparent reflecting walls. The formation of deposits on the quartz ceiling and their influence on radiative properties were taken into account. Figure 2.12 shows the measured outside, and calculated inside temperature distribution in the radial direction of the Aixtron planetary reactor.



Figure 2.12: Temperature distribution along the ceiling plate in radial direction, and measured temperature at a fixed position where the access for a thermocouple is given, (----) inner side of ceiling wall, (---) outer side, after Bergunde *et al.* [2.23].

GaAs layers were formed on a relatively hot ceiling, which lowered its temperature to a greater extent than was calculated for film thickness up to a few micrometres. When the GaAs film had a thickness over several micrometres, interference had a lower effect and absorption of thermal radiation was greater than for the quartz wall. This led to temperatures greater than that for a clean ceiling. When the ceiling was relatively cold, arsenic (As) condensed creating high reflectivity of the surface causing its temperature to drop dramatically, enhancing As deposition further. Using calculations and experimental data, an optimised adjustment of the cooling rate at the ceiling was found to minimise any deposits almost to zero. Low cooling rates at the surface reduced the As deposition. If the cooling rate was too low, the ceiling became hotter and a brownish GaAs film was deposited. Deposition rates of polycrystalline GaAs on the ceiling were calculated for various cooling rates. It was found that an almost exponential reduction of the deposited layer thickness occurred with a linear increase of the cooling rate. Also, thin GaAs deposits on the ceiling were expected to be self stabilising as they lower the ceiling temperature and hence the parasitic deposition rate. Thick deposits on the ceiling led to an unstable situation, increasing its temperature and the deposition rate due to rising radiation absorption. Figure 2.13 shows predicted ceiling temperature against GaAs thickness and measured ceiling temperature over time.



Figure 2.13: (a) Predicted temperature vs. thickness of deposited layers of polycrystalline GaAs on the ceiling of the Aix 200/4 planetary reactor (Figure 2.6, page 29); (b) Measured temperature at the top of the line tube in a horizontal reactor, vs. time, for a GaAs growth run starting from clean walls, after Bergunde's group [2.17].

2.3 Modelling kinetic-limited GaAs deposition

Many of the research investigations into GaAs growth have concentrated on diffusion of the reacting species within the gas stream. At process temperatures the mass transfer of the precursors dominates the growth at the substrate, whereas growth at the reactor wall is dominated by surface reactions where the temperature is much lower. This section will consider several investigations into rate-limited epitaxial growth and how the kinetic theory of GaAs deposition has developed over the years.

2.3.1 Surface reactions from TMGa and AsH₃

Tirtowidjojo and Pollard [2.7] developed a model which regarded many reaction processes. The purpose of the model was to use theoretical prediction to determine the dominant reaction pathways. Deposition was on a (111)Ga face surface, and the effect of temperature on the dominant gas phase and surface reaction pathways was investigated. At low temperatures, it was determined that some of the TMGa decomposed to dimethylgallium (DMGa) at ledge sites, with removal of 'CH₃ radicals from the adsorbed DMGa to form MMGa at the surface. This was the proposed ratelimiting reaction at 773K (500°C). AsH(s) and As(s) were determined to be formed at the surface by adsorbed AsH_x species ($1 \le x \le 3$), where sequential removal of H atoms occurs.

Reaction of MMGa(s) and AsH(s) or As(s) at the surface were proposed to form the GaAs deposit, with H(s) and CH₃(s) species adsorbed at the surface. CH₄ could then be formed from these adsorbed species removing them from the surface. The independence of the growth rate from p_{AsH_3} was considered by Denbaars and co-workers [2.4] to be observed from the absence of an As-species in the rate-controlling reaction. The effect of increasing the temperature in the model resulted in TMGa and DMGa decomposition in the gas phase becoming increasingly important. Also, the majority of 'CH₃ radicals react with H₂ or AsH₃ to form CH₄. Therefore, formation of C₂H₆ was negligible. It was postulated that the reaction between AsH₃ and 'CH₃ in the gas phase would be a driving force for the decomposition of TMGa. This accounted for the observed increased decomposition rate [2.3, 2.5] when AsH₃ was present with TMGa in the gas flow.

Increasing the temperature from 500°C to 727°C, the adsorption of MMGa and subsequent reaction with AsH(s) and As(s) became dominant. The production of MMGa increased with temperature and therefore there was more surface coverage of adsorbed MMGa(s). At 727°C surface coverage was approximately equal to the

adsorption equilibrium constant. Increasing the temperature further led to a decline in surface coverage due to desorption of the species becoming dominant.

It was found [2.7] that surface coverage of AsH(s) and As(s) was insensitive to temperature relative to MMGa(s). The model determined AsH(s) to form mainly from adsorbed $AsH_2(s)$, which is formed in the gas phase by reaction of AsH_3 with 'CH₃ and H[·] radicals in relatively large quantities. It is important to note in this study [2.7] that the model includes the adsorption of AsH_2 and AsH_3 . In further investigations, discussed later in this chapter, modelling of reaction mechanisms at the surface did not include adsorbed $AsH_2(s)$ or $AsH_3(s)$. This was because no kinetic data was available for their adsorption reaction. However, it is possible that reaction mechanisms may differ when deposition occurs at different types of surfaces. The surface used in this example [2.7] was from a substrate with a (111)Ga face. Adsorption of As-species will have a greater tendency to adsorb at this surface than at other surface orientations, for example (100) [2.5], where both Ga and As atoms are at the surface of the substrate. There was a large surface concentration of AsH_2 in the model [2.7] which led to regeneration of $AsH_3(s)$ and $AsH_3(g)$.

Larsen *et al.* [2.27] carried out investigations into the growth mechanism of GaAs and found that earlier publications contradicted their findings. They used D_2 instead of H_2 as carrier gas to study the reactions between TMGa and AsH₃ only with no reactions between the precursors and carrier gas. The gases leaving the reactor chamber were continuously sampled using a time-of-flight mass spectrometer. Data on the kinetics were obtained by measuring peak intensities against temperature. The temperatures at which the precursors decomposed were observed to be lower when both precursors were in the presence of one another, relative to their decomposition without the other precursor. This was agreeable with Nishizawa's group [2.3]. Figure 2.14 shows the ratio of TMGa to AsH₃ reacted from a range of V/III input concentration ratios.



Figure 2.14: Ratio of TMGa to AsH3 reacted, after Larsen and co-workers [2.27].

The plot shows the stoichiometry to be close to 1:1 in agreement with Ring and Schlyer [2.1], demonstrating simultaneous reaction of TMGa and AsH₃. This was consistent with the Langmuir-Hinshelwood and Eley-Rideal mechanism, but also with formation of a TMGa:AsH₃ adduct in the gas phase. It has been suggested [2.7] that homolytic decomposition of TMGa initiates GaAs decomposition, where 'CH₃ radicals are important for the decomposition of AsH₃. This would prevent the 'CH₃ radical reacting back with DMGa to form TMGa again. Another study by Larsen et al. [2.28] used toluene as a free radical scavenger to observe whether its presence or absence had any differing effects on TMGa decomposition. The results gave evidence that the reverse reaction of TMGa homolysis was unimportant. Reaction of AsH₃ with TMGa decomposition products was conceived to be possible, but a change in input concentration would not give a 1:1 stoichiometry in this study. Another radical scavenger, 1,4-cylcopentadiene (CDH), was used to test this concept. Figure 2.15 shows the decomposition of TMGa and AsH_3 with and without CDH. It can be seen that the CDH had no effect on the reaction.



Figure 2.15: (a) Decomposition of mixture of TMGa (\Box, \blacksquare) and AsH₃ (\supseteq) . Open symbols, no CHD: filled symbols, with CHD. (b) Decomposition of CHD: (•) with TMGa and AsH3: (•) CHD alone. For all experiments the concentrations were 0.5% TMGa, 0.5% AsH₃, and 8.0% CHD, after Larsen *et al.* [2.27].

It was found that the relative rates of reaction of \cdot CH₃ with AsH₃ and \cdot CH₃ with CDH at 425°C and at concentrations as in Figure 2.15 were 1/2.05 respectively, demonstrating competition for reaction with \cdot CH₃ between the two routes. At 450°C, all TMGa reacted. It was expected [2.27] that if the decomposition of TMGa and AsH₃ proceeded by a series of complex steps that included generation of \cdot CH₃ radicals, the addition of CDH would alter the partial pressure of \cdot CH₃. This would change the relative reaction rates, including that for TMGa pyrolysis.

The problem with CDH was that it is unstable and loses an H atom *para* to the radical carbon to produce benzene. The H atom has the ability to react with most of the species present in the system, which led to inconclusive results. Even so, Larsen *et al.* thought that the use of CDH demonstrated that the combined TMGa-AsH₃ pyrolysis occurred by a simple, concerted mechanism rather than by a series of gas phase processes.

GaAs layers were grown on microscope slides with V/III ratios of 2.0 and 0.5. Observation of the deposit under an optical microscope showed that Ga droplets had

formed on GaAs whiskers. Experiments were repeated using V/III = 25, with a maximum change in AsH₃ concentration being 4%. The reaction was pseudo-first order, with the TMGa concentration being the limiting factor. The decomposition of TMGa was monitored for high and low surface areas, and Arrhenius plots from the collected data showed the activation energy for the two cases were nearly identical. Larsen *et al.* concluded [2.27] that the rate determining step was heterogeneous at temperatures between 250 and 450°C.

The Langmuir-Hinshelwood mechanism was considered [2.27] as an alternative pathway. Here, TMGa and AsH_3 adsorb independently and then react. The adsorption of both species is assumed to be competitive and the rate law for the mechanism is expressed as

$$R = \frac{Sk_{s}b_{Ga}b_{As}P_{Ga}P_{As}}{(1+b_{Ga}P_{Ga})(1+b_{As}P_{As})}$$
(2.2)

Where S is the total concentration of surface sites, k_s is the rate constant for the surface reaction, b_i is the adsorption equilibrium constant for species i, and P_i is the partial pressure of species i. If the partial pressure of TMGa was kept constant, increasing the AsH₃ partial pressure caused the reaction order of AsH₃ to go from first to zero. Likewise, the same was the case for when the TMGa partial pressure was varied. This was agreeable with data collected by Reep and Ghandi [2.5] on the growth rate.

Larsen et al. [2.27] compared the above Equation (2.4) with the rate law expression for the adduct theory,

$$R = \frac{Sk_s b_{add} P_{Ga} P_{As}}{1 + b_{add} P_{Ga} P_{As}}$$
(2.3)

In this case, the product of the two precursor partial pressures, determine the rate. Whichever precursor pressure was varied, the same effect on the maximum rate would be observed. This is not so for the Langmuir-Hinshelwood mechanism, whereby the maximum rate depends upon the pressure and adsorption equilibrium constant of TMGa if the AsH₃ partial pressure is varied. The rate would be dependent upon AsH₃ when TMGa is varied, as observed by Reep and Ghandi. [2.5].

2.3.2 Multi-step reaction model of gas phase and surface reactions

Modelling rate-limited deposition of GaAs was developed from the work of Tirtowidjojo and Pollard [2.7] by investigating all possible gas phase and surface reactions involved in the growth process. This multi-step reaction approach used reaction rate parameters for each possible reaction. Mountziaris and Jensen [2.29] reported many rate parameters for gas phase and surface reactions, which included reactions leading to undesirable products as well as species involved in growth. The rate parameters are expressed in the Arrhenius equation,

$$k = A \cdot T^{\beta} \cdot \exp^{\frac{-E_a}{RT}}$$
(2.4)

The above equation expresses the rate constant k, using the rate parameters A, which is the pre-exponential factor, or frequency factor, and E_a , which is the activation energy. A temperature exponent is represented by beta (β). This was utilised by Chernov [2.30] to obtain a generalised expression for rate constants, where the measurement of the activation energy had not been achieved for the particular reaction. It was suggested that secondary surface reaction pathways could be responsible for carbon incorporation. The investigation focused on developing a detailed kinetic model of the epitaxial growth of GaAs from TMGa and AsH₃ using a carrier gas of hydrogen or nitrogen. They used a 2dimensional model of a hot wall tubular reactor to carry out kinetic analysis of chemical reactions. This neglected mass transport that had to be considered in actual 3dimensional MOCVD reactors. Reaction rate parameters for the critical elemental reaction steps were estimated using thermo-chemical methods and thermodynamic data with existing experimental observations. Mountziaris and Jensen [2.29] reported the gas phase reaction mechanism to revolve around the pyrolitic decomposition of TMGa to DMGa and MMGa, G_{15} and G_{16} in Table 2.1. The methyl radicals produced from TMGa decomposition can react with AsH₃ and H₂ (G_{19} and G_4 in Table 2.1), or abstract H atoms from TMGa or its decomposition by-products to produce Ga-carbene species (G_5 , G_6 and G_7 in Table 2.1). The carbene species are very reactive and are only intermediate species, and may react rapidly with H[•] to produce methylated Ga-species (G_8 , G_9 and G_{10} in Table 2.1), decomposition may also occur (G_{11} and G_{12} , Table 2.1). The Ga-carbene species were considered [2.29] not to affect the predictive growth rate, but important in the mechanism of carbon incorporation.

No.	Gas Phase Reaction	A	β	E_a / \mathbf{R}	Ref.
G ₁	${}^{\cdot}\mathrm{CH}_3 + \mathrm{H}^{\cdot} + \mathrm{M} \rightarrow \mathrm{CH}_4 + \mathrm{M}$	2.4×10^{22}	-1	0.0	[2.29]
G ₂	$\mathrm{H}^{.} + \mathrm{H}^{.} + \mathrm{M} \rightarrow \mathrm{H}_{2} + \mathrm{M}$	1.3×10^{16}	0.0	0.0	[2.29]
G ₃	$^{\cdot}\mathrm{CH}_{3}+^{\cdot}\mathrm{CH}_{3}\rightarrow\mathrm{C}_{2}\mathrm{H}_{6}$	2.0×10^{10}	0.0	0.0	[2.29]
G ₄	$H_2 + CH_3 \rightarrow CH_4 + H^{-1}$	2.9 x 10 ¹²	3.1	4378.0	[2.29]
G ₅	$Ga(CH_3)_3 + CH_3 \rightarrow Ga(CH_3)_2CH_2 + CH_4$	2.0 x 10 ¹¹	0.0	5032.2	[2.29]
G ₆	$Ga(CH_3)_2 + CH_3 \rightarrow Ga(CH_3)CH_2 + CH_4$	2.0×10^{11}	0.0	5032.2	[2.29]
G ₇	$Ga(CH_3) + CH_3 \rightarrow GaCH_2 + CH_4$	2.0×10^{11}	0.0	5032.2	[2.29]
G ₈	$Ga(CH_3)_2CH_2 + H^{\cdot} \rightarrow Ga(CH_3)_3$	$1.0 \ge 10^{14}$	0.0	0.0	[2.29]
G ₉	$Ga(CH_3)CH_2 + H^{\cdot} \rightarrow Ga(CH_3)_2$	$1.0 \ge 10^{14}$	0.0	0.0	[2.29]
G ₁₀	$GaCH_2 + H^- \rightarrow GaCH_3$	$1.0 \ge 10^{14}$	0.0	0.0	[2.29]
G ₁₁	$Ga(CH_3)_2CH_2 \rightarrow Ga(CH_3)CH_2 + CH_3$	3.5×10^{15}	0.0	29941.3	[2.29]
G ₁₂	$Ga(CH_3)CH_2 \rightarrow GaCH_2 + CH_3$	8.7×10^7	0.0	17813.8	[2.29]
G ₁₃	$Ga(CH_3)_3 + H^- \rightarrow Ga(CH_3)_2 + CH_4$	5.0×10^{13}	0.0	5032.2	[2.29]
G ₁₄	$Ga(CH_3)_2 + H^- \rightarrow GaCH_3 + CH_4$	5.0×10^{13}	0.0	5032.2	[2.29]
G ₁₅	$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3$	3.5×10^{15}	0.0	29941.3	[2.29]
G ₁₆	$Ga(CH_3)_2 \rightarrow GaCH_3 + CH_3$	8.7 x 10 ⁷	0.0	17813.8	[2.29]
G ₁₇	$GaCH_3 \rightarrow Ga + CH_3$	1.0×10^{16}	0.0	77600	[2.31]
G ₁₈	$AsH_3 + M \rightarrow AsH_2 + H^{-} + M$	3.2×10^{17}	0.0	37741.2	[2.30]
G ₁₉	$AsH_3 + H^- \rightarrow AsH_2 + H_2$	$1.0 \ge 10^{13}$	0.0	1006.4	[2.30]
G_{20}	$AsH_3 + CH_3 \rightarrow AsH_2 + CH_4$	3.9×10^{10}	0.0	855.5	[2.29]
G ₂₁	$AsH_2 + CH_3 \rightarrow H_2AsCH_3$	1.0×10^{13}	0.0	0.0	[2.30]
G ₂₂	$AsH_2 + H^- \rightarrow AsH + H_2$	1.0×10^{13}	0.0	1006.4	[2.30]
G ₂₃	$H_2AsCH_3 + H^- \rightarrow AsH_2 + CH_4$	3.0×10^{13}	0.0	5032.2	[2.30]
G ₂₄	$H_2AsCH_3 + CH_3 \rightarrow HAsCH_3 + CH_4$	$1.0 \ge 10^{10}$	0.0	5032.2	[2.30]
G ₂₅	$HAsCH_3 + H^- \rightarrow H_2AsCH_3$	3.0×10^{13}	0.0	5032.2	[2.30]

Table 2.1: Gas Phase Elemental Reactions with Arrhenius Parameters, presented in the Literature. E_a is the activation energy (J mol⁻¹), R is the gas constant (J K⁻¹ mol⁻¹) and A is the frequency factor (mol cm⁻³ s⁻¹), after Mountziaris and Jensen, Chernov, Mazumber and Lowry [2.29, 3.30, 2.31].

The increased production of atomic hydrogen and its reaction with TMGa and DMGa $(G_{13} \text{ and } G_{14} \text{ in Table 2.1})$ when using H₂ as a carrier gas was thought to enhance pyrolysis of TMGa relative to using N₂ as carrier gas. The release of the third methyl group to produce Ga was considered to take place at the surface based on bond strength estimates and experimental evidence [2.29]. Adduct formation from the reaction of TMGa with AsH₃ was considered, but it was concluded that arsenic adducts were not stable above 400°C and likely to decompose in the entrance of a conventional MOCVD reactor. The pressure and residence time are the other parameters that are important in determining the extent of precursor decomposition.

High temperatures, long residence times and high pressure were reported [2.29] to increase the importance of gas phase reactions, particularly G_4 , G_{13} and G_{14} . This is considered to have caused discrepancies between investigations carried out with different reactor configurations and parameters. Mountziaris and Jensen [2.29] considered an average steady state representation of an ideal surface where monolayer adsorption took place. It was thought that the growth mechanism was unlikely to be the same for different substrate orientations, which would be by step propagation or island formation (Figure 1.1, page 3) depending upon a given orientation. It was assumed the major Ga-species adsorbing to the surface was MMGa through dissociative adsorption of TMGa (S_{10} Table 2.2). This agreed with Denbaars *et al.* [2.4] who reported the growth rate of TMGa below 450°C to be small and heterogeneous decomposition of TMGa to be negligible, with two methyl radicals formed per TMGa molecule.

The decomposition of AsH_3 was proposed [2.10] to occur by a heterogeneous mechanism only, with the loss of the first H atom being the rate determining step. It was thought by Mountziaris and Jensen [2.29] that the mechanism was likely to be more complex, particularly when considering a mixture of TMGa and AsH_3 . Further reactions between adsorbed As- and Ga-species were expected. It was thought that AsH_3 was most likely to chemisorb dissociatively onto the GaAs surface releasing H₂, when considering the energy release when AsH_3 attaches onto a Ga surface atom. It was proposed that only H¹ and 'CH₃ radicals would chemisorb to the GaAs surface to any significant extent. Many elemental reaction steps were considered [2.29] in the investigation on three substrate orientations, (110)-surface, (111)-Ga surface and (100)-surface misoriented towards (110).

2.3.2.1 (110)-surface

Adsorption and dissociative adsorption of all the reactive species in the gas phase were considered to be involved. H· and 'CH₃ radicals were thought to be able to adsorb onto any surface site. Methyl-Ga species adsorbed onto As surface atoms and arsenic hydrides (AsH_x) (x = 1 - 3) adsorbed onto the Ga surface atoms. Carbon incorporation was thought to occur by a carbon replacing an As atom at the surface in the proposed mechanism [2.29], where the resulting attached species could react with other species to release the hydrocarbon in the form of CH₄. When the carbone carbon attached to two neighbouring Ga surface atoms, it was then thought to have become incorporated into the deposit (S₄₂, S₄₃, S₄₄ in Table 2.2). CH₄ was assumed to be formed at the surface due to abstraction reactions where gas phase species collide with surface species (S₁₈, S₁₉, S₂₃ and S₃₈ in Table 2.2).

Recombination reactions were also considered (S_{15} to S_{17} , S_{20} , S_{22} to S_{24} , S_{33} , S_{34} , S_{39} and S_{40} in Table 2.2) with removal of volatile by-products from the surface. The orientation of the surface was considered important because the recombination reactions required the species reacting with one another to be adsorbed at neighbouring surface sites. In the mechanism proposed of Mountziaris and Jensen [2.29] GaAs formation formed from the reaction between neighbouring Ga-species and As-species adsorbed at the surface. Nucleation was thought to be random, with growth occurring along a certain plane. Other layers were considered to form once the layer below was fully covered as each layer is parallel to and supported by the next layer below in the (110)-surface orientation.

No.	Reaction	A	β	E_a / R	Ref.
S ₁	$H^{\cdot} + s (s_{As} \text{ or } s_{Ga}) \rightarrow H(s)$	5.0 x 10 ¹²	0.5	0.0	[2.30]
S ₂	$\cdot CH_3 + s (s_{As} \text{ or } s_{Ga}) \rightarrow CH_3(s)$	1.3 x 10 ¹²	0.5	0.0	[2.30]
S ₃	$CH_3(s) \rightarrow CH_3 + s$	5.0 x 10 ¹²	0.5	0.0	[2.30]
S ₄	$GaCH_3 + s_{As} \rightarrow GaCH_3(s_{As})$	5.4 x 10 ¹¹	0.5	0.0	[2.30]
S ₅	$GaCH_3(s_{As}) \rightarrow GaCH_3 + s_{As}$	$1.0 \ge 10^{14}$	0.0	22644.7	[2.30]
S ₆	$GaCH_3(s_{As}) \rightarrow Ga(s_{As}) + CH_3$	2.6 x 10 ¹³	0.0	19071.9	[2.30]
S ₇	$Ga + s_{As} \rightarrow Ga(s_{As})$	5.9 x 10 ⁸	0.5	0.0	[2.31]
S ₈	$Ga(s_{As}) \rightarrow Ga + s_{As}$	$1.0 \ge 10^{13}$	0.0	22732.0	[2.31]
S ₉	$Ga(CH_3)_2 + s_{As} \rightarrow GaCH_3(s_{As}) + CH_3$	5.0 x 10 ¹¹	0.5	0.0	[2.30]
S ₁₀	$Ga(CH_3)_3 + s_{As} \rightarrow GaCH_3(s_{As}) + 2(\cdot CH_3)$	4.6 x 10 ¹¹	0.5	13084	[2.30]
S ₁₁	$AsH + s_{Ga} \rightarrow AsH(s_{Ga})$	5.6 x 10 ⁸	0.5	0.0	[2.31]
S ₁₂	$AsH(s_{Ga}) \rightarrow AsH + s_{Ga}$	$1.0 \ge 10^{14}$	0.0	20128.6	[2.29]
S ₁₃	$AsH_2 + s_{Ga} \rightarrow AsH(s_{Ga}) + H^{-1}$	5.6 x 10 ¹¹	0.5	0.0	[2.30]
S ₁₄	$AsH_3 + s_{Ga} \rightarrow AsH(s_{Ga}) + H_2$	5.6 x 10 ¹¹	0.5	6038.6	[2.30]
S ₁₅	$H(s_{Ga}) + H(s_{As}) \rightarrow H_2 + s_{Ga} + s_{As}$	$1.2 \ge 10^{17}$	0.0	10064.3	[2.29]
S ₁₆	$CH_3(s_{As}) + CH_3(s_{Ga}) \rightarrow C_2H_6 + s_{As} + s_{Ga}$	$1.0 \ge 10^{17}$	0.0	10064.3	[2.29]
S ₁₇	$H(s_{Ga}) + CH_3(s_{As}) \rightarrow CH_4 + s_{Ga} + s_{As}$	1.0 x 10 ¹⁷	0.0	5032.2	[2.29]
S ₁₈	$H^{\cdot} + CH_3(s) \rightarrow CH_4 + s$	$5.0 \ge 10^{12}$	0.5	0.0	[2.30]
S ₁₉	$CH_3 + H(s) \rightarrow CH_4 + s$	1.3×10^{12}	0.5	0.0	[2.30]
S ₂₀	$AsH(s_{Ga}) + H(s_{As}) \rightarrow AsH_2 + s_{Ga} + s_{As}$	$1.0 \ge 10^{22}$	0.0	10064.3	[2.30]
S ₂₁	$AsH(s_{Ga}) + H^{\cdot} \rightarrow AsH_2 + s_{Ga}$	5.0 x 10 ¹²	0.5	5032.2	[2.30]
S ₂₂	$AsH(s) + CH_3(s) \rightarrow As(s) + CH_4$	$1.8 \ge 10^{18}$	0.0	8554.7	[2.30]
S ₂₃	$AsH(s_{Ga}) + CH_3 \rightarrow As(s_{Ga}) + CH_4$	1.3 x 10 ¹²	0.5	5032.2	[2.30]
S ₂₄	$AsH(s_{Ga}) + AsH(s_{Ga}) \rightarrow 2As + H_2 + 2s_{Ga}$	$1.0 \ge 10^{17}$	0.0	17612.5	[2.29]
S ₂₅	$As_2 + 2s_{Ga} \rightarrow 2As(s_{Ga})$	$1.0 \ge 10^{29}$	0.0	15155	[2.31]
S ₂₆	$2As(s_{Ga}) \rightarrow As_2 + 2s_{Ga}$	$1.0 \ge 10^{18}$	0.0	15096.5	[2.29]
S ₂₇	$Ga(s_{As}) + CH_3(s_{Ga}) \rightarrow GaCH_3(s_{As}) + s_{Ga}$	$1.0 \ge 10^{17}$	0.0	5032.2	[2.30]
S ₂₈	$Ga(s) + CH_3 \rightarrow MMGa(s)$	1.3×10^{12}	0.5	0.0	[2.30]
S ₂₉	$As(s_{Ga}) + CH_3(s_{As}) \rightarrow AsCH_3(s_{Ga}) + s_{As}$	$1.0 \ge 10^{17}$	0.0	5032.2	[2.30]
S ₃₀	$As(s) + CH_3 \rightarrow AsCH_3(s)$	1.3×10^{12}	0.5	0.0	[2.30]
S ₃₁	$As(s_{Ga}) + H(s_{As}) \rightarrow AsH(s_{Ga}) + s_{As}$	$1.0 \ge 10^{18}$	0.0	5032.2	[2.30]
S ₃₂	$As(s) + H^{\cdot} \rightarrow AsH(s)$	$5.0 \ge 10^{12}$	0.5	0.0	[2.30]
S ₃₃	$GaCH_3(s_{As}) + As(s_{Ga}) \rightarrow GaAs + CH_3 + s_{Ga} + s_{As}$	5.0 x 10 ¹⁸	0.0	14744.2	[2.30]
S ₃₄	$GaCH_3(s_{As}) + AsH(s_{Ga}) \rightarrow GaAs + CH_4 + s_{Ga} + s_{As}$	$5.0 \ge 10^{18}$	0.0	14744.2	[2.30]
S ₃₅	$Ga(s_{As}) + As(s_{Ga}) \rightarrow GaAs + s_{Ga} + s_{As}$	$5.0 \ge 10^{18}$	0.0	14744.2	[2.30]
S ₃₆	$AsCH_3 + s \rightarrow AsCH_3(s)$	5.2×10^{11}	0.5	0.0	[2.30]
S ₃₇	$AsCH_3(s) \rightarrow AsCH_3 + s$	$1.0 \ge 10^{13}$	0.0	10064.3	[2.30]
S ₃₈	$AsCH_3(s) + H^{\cdot} \rightarrow As(s) + CH_4$	$5.0 \ge 10^{12}$	0.5	0.0	[2.30]
S ₃₉	$AsCH_3(s) + H(s) \rightarrow As(s) + CH_4$	$1.0 \ge 10^{18}$	0.0	5032.2	[2.30]
S ₄₀	$AsCH_3(s) + AsH(s) \rightarrow As_2 + CH_4$	$1.0 \ge 10^{17}$	0.0	7548.2	[2.30]
S ₄₁	$AsCH_3(s) + Ga(s) \rightarrow MMGa(s) + As(s)$	1.0 x 10 ¹⁷	0.0	5032.2	[2.30]

Continued

S ₄₂	$GaCH_2 + s_{As} + s_{Ga} \rightarrow GaC + H_2$	No data	No data	
S ₄₃	$Ga(CH_3)CH_2 + s_{As} + s_{Ga} \rightarrow GaC + \cdot CH_3 + H_2$	No data	No data	
S ₄₄	$Ga(CH_3)_2CH_2 + s_{As} + s_{Ga} \rightarrow GaC + 2(\cdot CH_3) + H_2$	No data	No data	

Table 2.2: Surface elemental reactions with Arrhenius parameters, presented in the literature. E_a is the activation energy (J mol⁻¹), R is the gas constant (J K⁻¹ mol⁻¹) and A is the frequency factor (mol cm⁻² s⁻¹), (s_{Ga}) and (s_{As}) refer to surface gallium and arsenic atoms respectively, (s) being either atom, after Mountziaris and Jensen, Chernov, Mazumber and Lowry [2.29, 3.30, 2.31].

2.3.2.2 (111)-Ga surface

For this substrate orientation, only Ga surface atoms are present on planar surfaces (known as terraces), with As surface atoms only existing at the edges (known as steps, Figure 1.1, page 3). Growth, including carbon incorporation, occurred at the step sites in the model. With the two different types of surface sites only coexisting at a step, recombination reactions involving H^{\cdot} and \cdot CH₃ became important. Other surface reactions were considered in addition to those in Table 2.2, and are given in Table 2.3.

No.	Reaction	Α	β	E_a / \mathbf{R}	Ref.
S ₁₅	$H(s_{As}) + H(s_{As}) \rightarrow H_2 + 2s_{As}$	1.2 x 10 ¹⁷	0.0	10064.3	[2.29]
S ₁₅	$H(s_{Ga}) + H(s_{Ga}) \rightarrow H_2 + 2s_{Ga}$	1.2 x 10 ¹⁷	0.0	15046.1	[2.29]
S ₁₆	$CH_3(s_{As}) + CH_3(s_{As}) \rightarrow C_2H_6 + s_{As} + s_{Ga}$	1.0 x 10 ¹⁷	0.0	8454.0	[2.29]
S ₁₆	$CH_3 (s_{Ga}) + CH_3 (s_{Ga}) \rightarrow C_2H_6 + s_{As} + s_{Ga}$	1.0 x 10 ¹⁷	0.0	10064.3	[2.29]
S ₁₇	$H(s_{As}) + CH_3(s_{As}) \rightarrow CH_4 + 2s_{As}$	1.0 x 10 ¹⁷	0.0	5032.2	[2.29]
S ₁₇	$H(s_{Ga}) + CH_3(s_{Ga}) \rightarrow CH_4 + 2s_{Ga}$	1.0 x 10 ¹⁷	0.0	5032.2	[2.29]
S ₃₃	$GaCH_3(s_{As}) + As(s_{Ga}) \rightarrow GaAs + \bullet CH_3 + s_{Ga} + s_{As}$	4.5 x 10 ¹⁷	0.0	10064.3	[2.29]
S ₃₄	$GaCH_3(s_{As}) + AsH(s_{Ga}) \rightarrow GaAs + CH_4 + s_{Ga} + s_{As}$	4.5 x 10 ¹⁷	0.0	12278.5	[2.29]

Table 2.3: Extra surface elemental reactions at the (111)-Ga surface, with Arrhenius parameters, after Mountziaris and Jensen [2.29].

Reactions $S_{15} - S_{17}$ were expected [2.29] to be similar for those in the (110)-surface with the only difference being that the species involved are adsorbed on the same type of surface site on the (111)-Ga surface. Rate of the growth reactions S_{33} and S_{34} differ due to the different arrangement of adsorbed film precursors at the surface. Ga surface atoms were more abundant than As surface atoms at the (111)-Ga orientation, but there were fluctuations of their relative amounts during growth, which was expected to depend upon conditions such as temperature and V/III ratio. Mountziaris and Jensen [2.29] assumed an average value of Ga-sites at the surface step to be 10% of total surface sites.

2.3.2.3 (100)-surface misoriented towards (110)

This surface is commonly used for devices. Here, Ga surface atoms are only considered to appear at the step, where growth and carbon incorporation are also considered [2.29] to occur. Initial distribution between As and Ga atoms depend upon the degree of misorientation. The additional reactions, with their rate parameters, to those displayed in Table 2.2 are as in Table 2.3. As mentioned earlier, Mountziaris and Jensen [2.29] used a 2-dimensional model of a hot wall tubular reactor for their simulation. The reactor was considered to be a horizontal quartz tube heated to uniform temperature. The substrate existed at the wall and covered the surface area from inlet to exhaust in the reactor chamber, where decomposition occurred. The reactants were considered dilute in a carrier gas, taking on its physical properties, axial dispersion in the flow was neglected. This simplified the mass transfer problem, allowing the flow and heat transfer problems to be solved independently and used in mass transfer calculations for different chemical kinetics. Considering mixtures of TMGa and AsH₃ in H₂, a simplified surface mechanism, valid for high V/III ratios (excess AsH₃) for temperatures below 800K, was expected to consist mainly of As-species covering the surface. Thermal desorption effects of As-species were determined to be insignificant. The material depositing on the wall was expected to also consist of polycrystalline GaAs, with solid As, liquid Ga and polymers being part of other possible depositing species.

2.3.2.4 Simulation of GaAs growth by MOCVD

Mountziaris and Jensen [2.29] thought their model was not directly comparable to growth in typical MOCVD reactors, but feasible when considering growth to be limited by chemical kinetics only. The major surface reactions considered were adsorption-desorption reactions of MMGa and AsH, including their reaction to form GaAs and CH₄. The growth rate strongly correlated with the surface reaction between AsH and MMGa

at a temperature of 527°C, which was the rate-determining step in the kinetically limited regime. The effect of changing the TMGa partial pressure was investigated using a susceptor temperature of 500°C. At low partial pressures, surface coverage of Gaspecies was low and all TMGa was eventually decomposed. At high partial pressures of TMGa, the surface saturated due to the high gas phase concentration and any further increase of the TMGa partial pressure made no difference, because the surface reactions were slow. The As saturated surface was more pronounced when changing the partial pressure of AsH₃ due to the V/III ratio with AsH₃ in excess. Therefore, no dependence of growth rate on AsH₃ partial pressure was observed under typical GaAs growth conditions, with V/III > 20.

It was reported that the major film precursor adsorbed on Ga surface atoms was AsH(s), with MMGa(s) dominating at As surface atoms, agreeing with Reep and Ghandi [2.5]. The surface was almost completely covered by these species at the low temperatures. An increase in substrate temperature reduced surface coverage [2.29] due to increased rate of growth reactions and desorption reactions at the surface. Carbon incorporation was observed to decrease with an increase in V/III ratio. This was explained by the increased availability of AsH₃ to react with \cdot CH₃, which may also react with TMGa, DMGa and MMGa to form carbones.

More recently, Mazumber and Lowry [2.31] have studied the effectiveness of existing models on epitaxial GaAs growth for use in predicting parasitic growth, in the kinetically limited regime. A modified mechanism was created from rate parameters reported by Tirtowidjojo and Pollard [2.7] and Mountziaris and Jensen [2.29]. The latter has been adopted by many other researchers modelling GaAs epitaxial growth, such as Ern *et al.* [2.32], Peskin and Hardin [2.33], and Chernov [2.30]. Simulations were carried out [2.31] in a simplified 2-dimensional geometry MOCVD system for low temperature growth. Results were produced for epitaxial growth by the different mechanisms with and without parasitic deposition. The same mechanism for deposition was used for deposition on the reactor walls. However, it may not be valid for parasitic deposition on reactor quartz walls due to the fact deposition is known to be non-

stoichiometric, and often polycrystalline or amorphous. It was observed during simulation that a significant amount of As(s) was adsorbed onto the surface at low temperatures. It was concluded that further investigation into parasitic growth with the use of multi-step reactions, including adsorption-desorption processes was imperative for modelling parasitic growth.

2.4 Summary

The parasitic deposition in commercial reactors has been minimised by using techniques such as cooling of the top plate in the horizontal reactor. Nevertheless it still occurs and over time the build up of the deposit decreases the process yield for device structures in the MOVPE industry. This requires reactors that normally operate around the clock every day to be shut down to enable the deposit in unwanted areas of the reactor to be cleaned allowing the process to continue.

It has been found that the parasitic growth changes the environment within the reactor causing drift from the required growth conditions for fabrication of device materials, which require abrupt surface changes achieved by accurate control of the growth parameters.

There is still a need to understand the nature of the parasitic deposition, and it has been proven that laser interferometry has the capabilities to monitor the growth rate on the reactor walls, as well as on the substrate where semiconductor materials are deposited.

Once initial nucleation on the reactor wall has been established, it is likely that the growth process follows the same mechanisms for parasitic growth as for epitaxial growth. A theoretical model using a steady state approximation is presented in Chapter 3 and discussed in Chapter 4, where multiple reaction mechanisms were considered. The model adopts rate parameters reported in the literature [2.7, 2.29, 2.31, 2.30] and predicts quantitatively the major deposition products obtained at kinetically limited temperatures.

The model was compared to real-time experimental growth rate data from laser reflectance measurements during deposition of GaAs in a simple quartz reactor tube. Temperatures reflected kinetic-limited growth found at reactor walls in horizontal commercial reactors. At these temperatures the growth rate is limited by surface reactions and it is proposed that a model of kinetic-limited deposition could be applied to any reactor configuration.

2.5 References

- [2.1] B.J. Schlyer, M.A. Ring, J. Organomet. Chem. 114, (1976) 9.
- [2.2] B.J. Schlyer, M.A. Ring, J. Organomet. Chem. 71, (1974) 25.
- [2.3] J. Nishizawa, T. Kurabayashi, J. Electrochem. Soc. 130, (1983) 413.
- [2.4] S.P. DenBaars, B.Y. Maa, P.D. Dapkus, A.D. Danner, H.C. Lee, J. Crystal Growth 77, (1986) 188.
- [2.5] D.H. Reep, S.K. Ghandi, J. Electrochem. Soc. 130, (1983) 675.
- [2.6] M.R. Leys, H. Veenvliet; J. Crystal Growth 55, (1981) 145.
- [2.7] M. Tirtowidjojo, R. Pollard, J. Crystal Growth 93, (1988) 108.
- [2.8] J. Nishizawa, T. Kurabayashi, Vacuum 41, (1990) 958.
- [2.9] M.A. Tischler, IBM J. Res. Develop. 34 (1990) 828.
- [2.10] K. Tamaru, J. Phys. Chem., 59, (1955) 777.
- [2.11] M.G. Jacko, S.J.W. Price, Can. J. Chem., 41, (1963) 1560.
- [2.12] H. Heinecke, E. Veuhoff, N. Putz, M. Heyen, P Balk, J. Elec. Mat. 13, (1984) 815.
- [2.13] M.R. Leys; Chemtronics 2 (1987) 155.
- [2.14] H.M. Manasevit, W.I. Simpson; J. Electrochem. Soc. 116 (1969) 1725.
- [2.15] P.M. Frijlink, J.L. Nicolas; J. Crystal Growth 115 (1991) 203.
- [2.16] T. Bergunde, F. Durst, L. Kadinski, Yu.N. Makarov, M. Schafer, M. Weyers; J. Crystal Growth 145 (1994) 630.
- [2.17] T. Bergunde, M. Dauelsberg, L. Kadinski, Yu.N. makarov, V.S. Yuferev, D. Schmitz, G. Strauch, H. Jurgensen; J. Crystal Growth 180 (1997) 660.
- [2.18] A.G. Thompson, R.A. Stall, W. Kroll, E. Armour, C. Beckham, P. Zawadzki, L. Aina, K. Siepel; J. Crystal Growth 170 (1997) 92.
- [2.19] C. Theodoropoulos, N.K. Ingle, T.J. Mountziaris, J. Crystal Growth 170, (1997) 72.
- [2.20] R. Takahashi, Y. Koga, K. Sugawara, J. Electrochem. Soc. 119, (1972) 1406.
- [2.21] H. Moffat, K.F. Jensen, J. Crystal Growth 77, (1986) 108.
- [2.22] J. Van de Ven, G.M.J. Rutten, M.J. Raaijmakers, L.J. Giling, J. Crystal Growth 76, (1986) 352.
- [2.23] T. Bergunde, D. Gutsche, L. Kadinski, Yu. Makarov, M. Weyers; J. Crystal Growth 146, (1995) 564.
- [2.24] T. Bergunde, M. Dauelsberg, L. Kadinski, Yu.N. Makarov, M. Weyers, D. Schmitz, G. Strauch, H. Jurgensen; J. Crystal Growth 170, (1997) 66.

- [2.25] L. Kadinski, Yu.N. Makarov, M. Schäfer, M.G. Vasil'ev, V.S. Yuferev, J. Crystal Growth 146, (1995) 209.
- [2.26] F Durst, L Kadinski, Yu N Makarov, M Schäfer, MG Vasil'ev, VS Yuferev, J. Crystal Growth 172, (1997) 389.
- [2.27] C.A. Larsen, S.H. Li, N.I. Buchan, G.B. Stringfellow, J. Crystal Growth 102, (1990) 126.
- [2.28] C.A. Larsen, S.H. Li, N.I. Buchan, G.B. Stringfellow, J. Crystal Growth 102, (1990) 103.
- [2.29] T.J. Mountziaris, K.F. Jensen, J. Electrochem. Soc. 138, (1991) 2426.
- [2.30] "Handbook of Crystal Growth", D.T.J. Hurle, Elsevier, (1994) 459.
- [2.31] S. Mazumber, S.A. Lowry, J. Crystal Growth 224, (2001) 165.
- [2.32] A. Ern, V. Giovangigli, M.D. Smooke, J. Comp. Phys. 126, (1996) 21.
- [2.33] A.P. Peskin, G.R. Hardin, J. Crystal Growth 186, (1998) 494.

3.0 Experimental and theoretical method

3.1 Gas system

The gas system for the MOCVD reactor where experiments were carried out was manufactured by Electrogas Ltd. The initial design proposed by Electrogas is shown in Figure 3.1, the main problem with this design was that during idle status of the MOCVD reactor, the precursor lines were not able to be purged with N_2 . Purging prevents lines from collecting moisture and also avoids corrosive precursors being stationary in the lines. This would also make maintenance work on the gas lines dangerous, as AsH₃ is very toxic and TMGa is extremely flammable as well as toxic.



Figure 3.1: Original illustration of the gas system for carrying the precursors to the reactor chamber.

The changes that were made to the design are shown in Figure 3.2. The rest of the system design was as in Figure 3.1, where the exhaust line of the reactor led to the valve

labelled vacuum, before joining with the vent line which lead to the vacuum pump or straight to the vent (valve labelled atmospheric).

The altered design included a line for N_2 to flow through valve 13 (Figure 3.2) to purge the AsH₃ line. Valve 4 was the route for the H₂ carrier gas to flow to the reactor, which would pick up the precursors at valves 15 and 17. Even though this design was accepted and used for the process, it became evident that the TMGa line still did not have a dedicated purge line. To overcome this, the N₂ had to be directed through valves 1 and 2 along the He line or through valves 4 and 5 along the H₂ line when the system was idle. The latter method was adopted because the H₂ line on top of the reactor cabinet had an isolation valve which could be closed when H₂ was not in use. The carrier gas H₂ was passed through a H₂ purifier, employing a palladium membrane that only H₂ molecules could diffuse through. In addition, all input gas lines were fitted with non-return valves.



Figure 3.2: Illustration of final design of the gas system.

A measured amount of AsH₃ was supplied from a 1.2 L cylinder using the differential pressure between the cylinder and the reactor chamber, with control of flow using a MFC. The negative pressure of the reactor chamber resulted in the AsH₃ molecules desorbing from an activated carbon media in the arsine cylinder. The cylinder included its own pneumatic valve which had to be incorporated into the valve electrics. This valve is not shown in Figure 3.2 and would be positioned to the left of valve 6 on the illustration. A safety circuit was put in place to prevent backfill into the cylinder should a problem arise within the system, such as a leakage. As the cylinder was filled with AsH₃ by its adsorption to a carbon matrix within the cylinder, the cylinder was able to be filled and stored at negative pressure (0.866 atm). Supply of AsH₃ would only be initiated in the growth procedure when the MOCVD system had been reduced to the growth pressure of 0.197 atm.

The safety circuit was connected to the MFC controlling the flow rate of AsH_3 to the reactor. When the positive flow reduced close to zero, the safety circuit would activate and close the cylinder valve. This prevented a negative flow of AsH_3 and H_2 into the cylinder. If H_2 or any other compounds other than AsH_3 entered the cylinder, it would be impossible to supply an accurate concentration of the precursor required for reaction.

AsH₃ detectors were used around the system in case of the possibility of a leak. These were digital satellite detectors supplied by ATMI. Four AsH₃ detectors were placed at various points on the equipment where leakage of AsH₃ was most likely to occur. This included the cabinet where the AsH₃ cylinder was stored, and at a suspended position over the point where the reactor tube fitted to the gas manifold (reactor inlet). The third position was at the end of the exhaust near the vent to ensure the gas had been adsorbed in the active carbon trap, a similar matrix to the cylinder. Finally, another detector was placed on the top of the reactor cabinet near to where the operator's head would be when entering to the cabinet. The detectors had audio alarm and LED signals that were connected to a visual display outside the laboratory to show the status of each detector from a safe position. Each detector was connected to its own display unit on top of the reactor cabinet for the operator to monitor. When any AsH₃ alarm(s) activated, all

valves on the system would close to isolate the leak and to prevent further supply of AsH₃ from the source to the position of leakage. The cabinet was extracted and any leak would be contained.

3.1.1 Experimental parameters

The experimental and parameter set-up were reproduced from those utilized by Bergunde et al. [3.1] to represent conditions in a commercial reactor. The substrate in the Aixtron reactor used by Bergunde and co-workers (Figure 2.6, page 29) was positioned from 3.5 to 11 cm in the radial direction from the inlet. This area was heated and radiation towards the ceiling by free convection was observed [2.1, 2.2]. Maximum growth occurred at 6 cm in the radial direction from the inlet (Figure 2.11, page 43). Growth started at 3 cm and decreased from the maximum more gradually to the edge of the reactor. Precursor depletion was observed to play a major part in the decrease in growth rate toward the exhaust of the reactor. The edge of the reactor tube to where the ceiling deposit was measured was 12 cm. The maximum growth rate at the ceiling was at 6 cm in the radial direction from the inlet (Figure 2.11, page 43). In the proposed reactor set-up for this study (Figure 3.3) the temperature of the reactor chamber was achieved by using a resistance heated furnace. This surrounded a 20 cm section at the centre of the reactor chamber, giving a constant and uniform temperature distribution at temperatures relating to calculated [3.1, 3.2] ceiling temperatures in the Aixtron reactor. The kinetics of species deposition in this set-up can be expected to be more consistent along the heated zone.


Figure 3.3: Experimental set-up of the quartz reactor tube illustrating the hot zone within the furnace and the laser interferometer.

In the system used by Bergunde *et al.* [3.1, 3.2], the radiating heat in the gas phase was greater than the temperature of the gas phase in the reactor tube, because the ceiling temperature in the Aixtron reactor was a result of a cooling mixture of H_2/Ar . This means that there could be different species reaching the ceiling due to the higher gas temperatures, although these species may only be significant in the diffusion zone of the Aixtron reactor.

The flow velocity was at its maximum at the inlet and decreased towards the exhaust. The distance from the inlet to the wafer edge nearest the inlet was 3.5 cm, and the distance to the wafer edge nearest the outlet was 11 cm (a), as illustrated in Figure 3.4. The distance from the inlet to the wafer centre was 7.25 cm (b), with the flow spreading 360° from the inlet over the wafers. The flow velocity at a specific radial position was calculated by division of the total flow by the surface area of the moving gas with the dimensions of the reactor.



Figure 3.4: Illustration of flow direction in the Aixtron multi-wafer reactor.

The flow velocities have been calculated using the same method as above for the first and second edge of the wafer the gas reaches, and for the position of maximum growth rate. The surface area of the flow at the wafer centre was $2\pi r x$ depth, where r was equal to distance (b) (Figure 3.4). The calculated flow velocity, at different radial positions for the total flow in the Aixtron reactor of 17.2 slm can be used to calculate the equivalent total flow and residence times in the reactor tube. These are presented in the table below and in Table 3.1 and Figure 3.5.

Radial Position in Aixtron reactor	Distance (cm)	F _{vel} at 200 mbar (cm s ⁻¹)	F _{tot} in quartz tube (sccm)	Residence time of gas in quartz tube (s)
1 st Wafer Edge	3.5	44.11	2560	0.45
Maximum Growth	6	25.74	1490	0.78
Wafer Centre	7.25	21.32	1240	0.94
2 nd Wafer Edge	11	14.01	812.9	1.43

Table 3.1: Equivalent total flow and residence time in the quartz reactor tube for experiments reported in this thesis from the total flow of 17.2 slm used in the Aixtron reactor.



Figure 3.5: Calculated flow velocity in the radial direction of the Aixtron planetary reactor from a total flow of 17.2 standard litres per minute (slm).

The flow velocity used for the MOCVD of this research was related to the maximum flow rate used by Bergunde's group reflecting the flow that gave maximum deposition in their experiments. When residence times in the reactor chamber were low (large flow velocities, F_{vel}), the deposition process was limited by the kinetics as increased forced convection of the flow reduces the diffusion time. This project concentrated on kinetic-limited GaAs deposition for low temperature. Therefore the calculated flow within the reactor tube used in this study reflected a large total flow within the Aixtron reactor [3.2], which was $F_{tot} = 17.2$ slm. This is equivalent to 286.67 standard cm³ s⁻¹, or 1455.18 cm³ s⁻¹ at 0.197 atm (200 mbar). The depth of the Aix-2400 reactor was 1.5 cm. At the radial position of 6 cm the surface area of the moving gas was calculated.

$$2\pi r \times depth = 2 \times \pi \times 6 \times 1.5 = 56.55 \,\mathrm{cm}^2 \tag{3.1}$$

A F_{tot} of 17.2 slm = 286.67 standard cubic centimetres per second (sccs). The flow velocity (F_{vel}) at 6 cm in the radial direction at atmospheric pressure was:

$$\frac{286.67}{56.55} = 5.05 \,\mathrm{cm \, s^{-1}}.\tag{3.2}$$

The flow velocity at 0.197 atm is represented for this radial position in Table 3.1. The reactor tube diameter used in this research was 2.50 cm, the area of the inlet is therefore 4.91 cm^2 .

$$F_{tot} = F_{vel} \times \pi \times r^{2},$$

$$5.05 \times \pi \times 1.25^{2} = 24.8 \text{ cm}^{3} \text{ s}^{-1},$$

$$F_{tot} = 1.49 \text{ slm}.$$
(3.3)

The residence time in the heated zone (20 cm) was expressed by $\frac{20}{F_{vel}}$.

GaAs deposition was carried out in a horizontal quartz reactor tube with TMGa and AsH₃ as precursors. Experiments were carried out at temperatures ranging from 400°C to 500°C, using a resistance heated furnace. A thermocouple placed at the furnace centre, touching the outer wall of the quartz tube, was used for temperature control. A second thermocouple was placed inside the reactor tube, positioned at the top near the centre, to measure the gas temperature (Figure 3.3). A total pressure of 0.197 atm and flow of 1.49 slm using H₂ as carrier gas were employed. V/III ratios of 10, 30 and 50 were used, keeping p_{AsH_3} constant. The partial pressure of trimethylgallium (TMGa) was equal to 0.0168 atm, at a reactor pressure of 0.197 atm, in the work of Bergunde and coworkers [3.2]. This is equivalent to 8.52 $\cdot 10^{-5}$ atm at standard pressure (STP).

The saturated vapour pressure (SVP) of TMGa can be calculated from the equation:

$$log (svp) = 8.07 - \frac{1703}{T}.$$
(3.4)
At 273 K the SVP = 0.089 atm.

The bubbler flow for TMGa can be calculated from the equation:

$$F_{bub_{(TMGa)}} = \frac{F_{tot} \times conc}{svp} \times \frac{p_{atm}}{p_{react}}$$

$$F_{bub_{(TMGa)}} = \frac{1.49 \times 8.52 \times 10^{-5}}{0.089} \times \frac{1}{1} = 0.001 \, \text{slm.}$$
(3.5)

 F_{bub} at standard pressure was 1.4 sccm, at 0.197 atm this pressure is equal to $7 \cdot 10^{-3}$ L min⁻¹.

The ideal gas law was used to calculate the number of moles per minute using volume of gas per minute at a temperature of 294 K, the partial pressure of TMGa was equal to $1.678 \cdot 10^{-5}$ atm, and the gas constant was $8.20578 \cdot 10^{-2}$ L atm K⁻¹ mol⁻¹.

$$n = \frac{0.007 \times 1.678 \times 10^{-5}}{294 \times 8.20578 \times 10^{-2}} = 1.85 \cdot 10^{-9} \text{ moles min}^{-1}.$$
(3.6)

Molar (initial) concentration = $7.0 \cdot 10^{-10}$ mol. cm⁻³.

Consumption of TMGa at STP from a one hour growth run can be calculated:

$$F_{tot} \cdot \text{conc.} \cdot \text{growth time} = \text{volume (L)}, \qquad (3.7)$$
$$1.49 \times 8.52 \times 10^{-5} \times 60 = 0.008 \text{ L}.$$

One mole of gas occupies 22.4 L at STP (273 K, 1 atm).

$$\frac{0.008}{22.4} = 3.40 \times 10^{-4} \text{ moles.}$$
(3.8)

The molecular weight of TMGa is 114.825.

 $3.40 \cdot 10^{-4} \times 114.825 = 0.039 \text{ g.}$ (3.9)

For a one hour growth run 39 mg of TMGa was used.

When V/III ratio used was 50, with TMGa F_{bub} equal to 1.4 sccm and F_{tot} equal to 1.49 slm. The p_{AsH_3} was calculated as $4.26 \cdot 10^{-3}$ atm at STP.

$$F_{AsH_3} = 4.26 \times 10^{-3} \times 1.49 = 0.0064 \,\text{slm} \,(6.4 \,\text{sccm}).$$
(3.10)

At 0.197 atm, the F_{AsH_3} will be 22.8 cm³ min⁻¹. Using Equation 3.11, the number of moles per minute can be calculated:

$$n = \frac{0.0228 \times 8.39 \times 10^{-4}}{294 \times 8.20578 \times 10^{-2}} = 7.93 \times 10^{-7} \,\text{mol. min}^{-1}.$$
(3.11)

Molar (initial) concentration = $1.3 \cdot 10^{-8}$ mol. cm⁻³.

The arsine precursor is stored at room temperature which is close to the standard ambient temperature and pressure (298 K, 0.987 atm). One mole of gas at STP occupies 24.789 L. Using Equations 3.12 - 3.14 the mass of arsine consumed for a two hour growth run can be calculated:

$$1.49 \times 4.26 \times 10^{-3} \times 60 = 0.38 \text{ L},$$
 (3.12)

$$\frac{0.38}{24.789} = 1.5 \times 10^{-2} \text{ moles}, \tag{3.13}$$

$$1.5 \cdot 10^{-2} \times 114.825 = 1.17 \text{ g.}$$
 (3.14)

Using the V/III ratio of 50 as above, the precursor and carrier gas flow in the reactor tube can be calculated for the different flow velocities at the different radial positions in the Aixtron reactor. Table 3.2 uses flow velocities calculated from the total flow in the Aixtron reactor of 17.2 slm.

Radial Position in Aixtron reactor	F _{TMGa} in quartz tube (sccm)	F _{AsH3} in quartz tube (sccm)	F _{H2} in quartz tube (sccm)
1 st Wafer Edge	2.5	10.9	2547
Maximum Growth	1.4	6.3	1482
Wafer Centre	1.2	5.3	1234

Table 3.2: Precursor and carrier gas flow in quartz reactor tube.

The flow used in experimentation was related to the observed [3.1, 3.2] maximum growth from experiments carried out by Bergunde's group. It was anticipated that the other flows representing the flow at the first wafer edge and wafer centre would also be adopted to compare the kinetic process between each flow.

3.2 In situ reflectance monitoring

The deposition rate was measured in situ using reflectance interference from a laser positioned near normal incidence above the reactor tube. Initially, a 50 mW, 635 nm diode laser was used to monitor the growth rate during experiments. No change in the reflectance intensity was observed during experiments, the wavelength of the laser was changed to 980 nm. Quartz and GaAs are transparent at this wavelength and had been used by Weeks and co-workers [3.3], and proven to give interference data of AlGaAs deposition on an Aix-2400 multi-wafer reactor. The reflection intensity from the quartz tube was found to be small, so a quartz wafer was placed inside the tube, resting on the walls and aligned with the incident beam. When the wafer was aligned with the beam, the signal was observed to increase significantly. The reflectance signal from a clean tube and wafer was expected to be from three points of which the beam came into contact with. This included the bottom surface of the tube in addition to the top surface and quartz slide. With deposition of GaAs, interference of the laser reflectance changed with the change in thickness of the deposit. The change in interference altered the reflectance intensity recorded by a photo-detector in the reflectometry casing that also housed the laser diode. Figure 3.6 illustrates interference of reflected wavelengths from the growing film surface.



Figure 3.6: Reflection interference oscillations from growing GaAs surface during MOCVD. The illustration is for clearer representation, normal incidence was employed.

Reflection waves interfered with one another to give a combined reflection intensity recorded by the detector. Over time the recorded reflectance intensity gave oscillatory curves as an interferogram, this was because the interference changed between constructive and destructive interference. Figure 3.7 shows the effect of constructive and destructive interference, which is the result of the change in interference due to the growing surface illustrated in Figure 3.6.



Figure 3.7: Constructive and destructive interference from reflection oscillations.

When an incident beam travels from one medium to another, some of the radiation is reflected, while the rest of the beam is transmitted through or absorbed by the medium. When GaAs was deposited onto the quartz surface within the reactor, a portion of the laser beam was reflected from the surface of quartz or GaAs and the quartz-GaAs interface, with interference between the reflections, which changes due to growth of the material. Interference of the reflected beams is affected by the thickness of the reflecting film. The refractive indexes of the media the laser incident beam passes through, and is reflected, are listed below.

Air, vacuum or carrier gas, $n_0 = 1$. Quartz, $n_1 = 1.54$ at 980 nm. GaAs, $n_2 = 3.3$ at 980 nm. The refractive indexes of the above media are as follows: $n_0 < n_1 < n_2$.

The optical path length difference can be represented by the equation below.

 $\Gamma = 2 \times d \times n_2$.

(3.15)

Where d is the thickness and n_2 is the refraction index of the GaAs deposit. When the incident beam travels from one medium to another medium with a higher refractive index, the reflecting beam will shift in phase by 180°. When no phase change, or two phase changes occurs, Γ can be represented by the equation below,

$$m\lambda = 2 \times d \times n_2. \tag{3.16}$$

This will give rise to constructive interference. Here, m is an integer, and represents whole wavelengths. If a phase change occurs from one surface, destructive interference will occur, and is represented by,

$$(m - \frac{1}{2})\lambda = 2 \times d \times n_2.$$
(3.17)

For GaAs, if m = 1 (λ), constructive interference will occur when the optical thickness is 148.48 ± 5 nm. The error considered in the thickness takes into account a 2 nm drift expected to be present in the laser diode, and also ±0.1 associated with the refractive index. The refractive index changes with temperature, composition of the depositing material, with a slight variation at different wavelengths. This was not measured, and so the error was estimated. When a phase change occurs, the thickness will be 74.24 ± 2.3 nm ($\frac{1}{2}\lambda$). Assuming all positions of quartz surfaces inline with the incident beam experience the same temperature, the interference of the reflectance can be calculated.

Figure 3.8 shows the change in reflectance intensity obtained from a clean tube and wafer when a non-reflective strip was used to mask reflectance from the different positions inline with the incident beam. The incident beam of the laser reflected from three positions as shown in Figure 3.8, when a calibration experiment of the laser reflectance was carried out for a clean quartz tube and slide. The laser intensity was kept constant for each experiment after this calibration. The quartz reactor tube and slide were aligned with the laser incident beam before each run so that the reflectance intensity signal produced the best sensitivity to change where recorded data fitted within

the arbitrary unit values in the range 0 to 10. The laser was initially aligned with the quartz tube, which was reflected at intensity 2.4 to 2.9 (a.u.). With the addition of a quartz wafer, the signal increased to between 6 and 7 (a.u.).



Figure 3.8: Reflection from top and bottom surfaces of a clean quartz tube with aligned clean quartz slide.

3.2.1 Absolute reflectance model

The absolute reflectance model was based on Figure 3.8, which shows the reflection intensity from the three different points that reflected the laser beam. Using the refractive index for quartz and air, the percentage reflectance that would occur from each point of reflection can be calculated and then fitted to the intensity values for the reflection from each surface aligned with the laser. Absolute reflectance has a value of 1.0 for total reflection. Quartz and GaAs are transparent at 980 nm, therefore most of the incident beam passes through each medium, with only a relatively small percentage of the beam intensity being reflected. The intensity of the incident beam becomes less and less with each pass through a medium until transmitted intensity is negligible. The equations below show the percentage of the incidence beam that is not transmitted for different surface interfaces.

the arbitrary unit values in the range 0 to 10. The laser was initially aligned with the quartz tube, which was reflected at intensity 2.4 to 2.9 (a.u.). With the addition of a quartz wafer, the signal increased to between 6 and 7 (a.u.).



Figure 3.8: Reflection from top and bottom surfaces of a clean quartz tube with aligned clean quartz slide.

3.2.1 Absolute reflectance model

The absolute reflectance model was based on Figure 3.8, which shows the reflection intensity from the three different points that reflected the laser beam. Using the refractive index for quartz and air, the percentage reflectance that would occur from each point of reflection can be calculated and then fitted to the intensity values for the reflection from each surface aligned with the laser. Absolute reflectance has a value of 1.0 for total reflection. Quartz and GaAs are transparent at 980 nm, therefore most of the incident beam passes through each medium, with only a relatively small percentage of the beam intensity being reflected. The intensity of the incident beam becomes less and less with each pass through a medium until transmitted intensity is negligible. The equations below show the percentage of the incidence beam that is not transmitted for different surface interfaces.

Clean quartz: at tube wall and at slide.

$$\mathbf{R} = \left(\frac{\mathbf{n}_1 - \mathbf{n}_0}{\mathbf{n}_1 + \mathbf{n}_0}\right)^2 = 0.033 \ (3.3 \ \%). \tag{3.18}$$

With GaAs film:

At interface,
$$R = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 = 0.132 \ (13.2 \ \%).$$
 (3.19)

At GaAs surface,
$$R = \left(\frac{n_2 - n_0}{n_2 + n_0}\right)^2 = 0.286 \ (28.6 \ \%).$$
 (3.20)

Figure 3.9 illustrates the reflection of a laser from a quartz tube with GaAs deposited on it. The beam was considered to be near normal incidence to the reflecting surface of the tube and deposit, the representation in Figure 3.9 is for a clearer illustration.





Below is a diagram (Figure 3.10) of a cross section of the quartz tube and quartz slide without a GaAs deposit, showing the reflection pattern of the incidence beam from the laser diode, which is near normal incidence to the tube. The reflection and transmission is represented by arrows, their orientation in the diagram does not represent their reflected direction. The arrows are arranged to allow for a clearer illustration.



Figure 3.10: Cross section of reactor tube and slide with reflectance behaviour illustrated, where T represents transmittance and R represents reflection.

The calculated absolute reflectance (abs. ref.) from each quartz/air interface is a product of the transmitted incidence probe and the calculated reflectance percentage from Equation 3.19 above. Table 3.3 shows the method for the calculated reflectance that is detected from the top of the quartz tube and quartz slide.

R_x/T_y	Equation	abs. ref.
R_1	Equation 3.19	0.033
T_1	(1 – 0.033)	0.976
R ₂	T ₁ x 0.033	0.032
R ₃	R ₂ x 0.033	0.0011
T ₂	$R_2 - R_3$	0.031
T ₃	$T_1 - R_2$	0.935
R ₄	T ₂ x 0.033	0.031
R ₅	R ₄ x 0.033	0.001
T_4	$R_4 - R_5$	0.030
R ₆	T ₄ x 0.033	0.00099
T ₅	$R_4 - R_6$	0.029
T ₆	$T_2 - R_4$	0.904
R ₇	T ₆ x 0.033	0.0298
R ₈	R ₇ x 0.033	0.00098
T ₇	$R_7 - R_8$	0.0288
R ₉	T ₇ x 0.033	0.00095
T ₈	$T_7 - R_9$	0.0279
R ₁₀	T ₈ x 0.033	0.00092
T 9	$T_8 \ge R_{10}$	0.027

Table 3.3: Calculated absolute reflectance from the top tube wall and quartz slide using Equation (3.19). T = transmittance and R = reflection.

The calculated reflectance from:

Top of the quartz tube = $R_1 + T_2 = 0.064$ (abs. ref.).

Quartz slide = $T_5 + T_9 = 0.056$ (abs. ref.).

Bottom of the quartz tube = $T_{14} + T_{20} = 0.049$ (abs. ref.).

From Figure 3.8, reflection intensity from the quartz wafer was 4.42 (a.u.), which is equivalent to 0.056 abs. ref. This was calculated by tilting the wafer after it was aligned with the laser beam so that no reflection from it was detected. When aligned, it was assumed that no scattering from the quartz wafer surface occurred. The reflectance intensity of 0.056 (abs. ref.) is equivalent to 5.6% of total reflection, and was used to calibrate the reflectance scale.

Total reflection =
$$\frac{4.42}{0.056} = 78.93$$
 (a.u.). (3.21)

If no scattering was occurring at the top quartz wall, reflectance intensity would be observed on the calibration graph to be:

$$0.064 \times 78.93 = 5.05$$
 (a.u.). (3.22)

However, the observed reflectance intensity was 0.61 (a.u.), which was due to the majority of the reflection being scattered from the curved surface of the top tube wall, where the detector cannot record the intensity. Absolute reflectance of observed reflectance intensity:

$$\frac{0.61}{5.05} \cdot 0.064 = 0.0077 \,(\text{abs. ref.}). \tag{3.23}$$

This is equivalent to 12.08% of the laser beam reflection from the top tube wall that was detected. Absolute reflectance intensity may be calculated for the bottom tube wall reflection in the same way:

$$0.049 \times 78.93 = 3.89$$
 (a.u.), (3.24)

$$\frac{0.52}{3.89} \times 0.049 = 0.0066 \,(\text{a.u.}) \tag{3.25}$$

This is equivalent to 13.34% of the reflected laser beam from the bottom tube wall, the rest of the reflection being scattered. The internal reflection from the reflectometer (1.08 a.u.) within the casing that also houses the laser diode was equivalent to 0.0137 (abs. ref.). The observed overall reflection from the calibration graph 6.63 (a.u.) was equal to 0.084 (abs. ref.).

Calculated absolute reflectance from each point of reflection will not change with laser beam intensity, allowing the above model to be used with variable laser intensities. Figure 3.11 is a diagram of the quartz tube and slide with a GaAs deposit. As in Figure 3.10, reflection and transmission at each interface is represented by arrows.



Figure 3.11: Cross-section of reactor tube and substrate with GaAs deposit present, with reflectance behaviour illustrated. T = transmittance and R = reflection.

The calculated reflectance from each surface and interface is a product of the transmitted incidence probe and the calculated reflectance percentage from each medium interface from Equations 3.19, 3.20 and 3.21. Table 3.4 shows the method for the calculated reflectance that was detected from the top of the quartz tube with GaAs deposit.

R_x / T_y	Equation	Value
R ₁	Equation 3.19	0.033
T ₁	(1 - 0.033)	0.976
R ₂	T ₁ x 0.132	0.128
R ₃	R ₂ x 0.033	0.004
T ₂	$R_2 - R_3$	0.124
T ₃	$T_1 - R_2$	0.840
R ₄	T ₃ x 0.286	0.240
R ₅	R ₄ x 0.132	0.032
T ₄	$R_4 - R_5$	0.208
R ₆	T ₄ x 0.033	0.0069
T ₅	$R_4 - R_6$	0.201

Table 3.4: Calculated absolute reflectance from top tube wall using Equations (3.19 - 3.21).

The calculated absolute reflectance from:

Top of the quartz tube = $R_1 + T_2 + T_5 = 0.358$ (abs. ref.). Quartz slide = $T_9 + T_{14} + T_{20} + T_{27} = 0.185$ (abs. ref.).

Bottom of the quartz tube = $T_{35} + T_{44} + T_{54} = 0.015$ (abs. ref.).

Total reflection from the reactor wall and quartz slide is 0.559 (a.r.), this would be equivalent to 45.2 (a.u.) when including internal reflection within the reflectometer. Following Equations (3.27 - 3.30), expected absolute reflectance from the top and bottom tube wall would be 0.043 (a.r.) and 0.002 (a.r.) respectively. The observed total reflection, including internal reflection from the reflectometer, would then be expected to be:

0.043 + 0.185 + 0.002 + 0.0137 = 0.2437 (abs. ref.). 0.2437.78.93 = 19.24 (a.u.)

Table 3.5 is a summary of calculated absolute reflectance from using Figure 3.8. It shows the measured reflectance intensity from a clean quartz surface from the three different surfaces that reflect the laser beam. Predicted arbitrary units for reflectance intensity, with GaAs deposited on the quartz surface, are also given from the absolute reflectance model.

	Top tube wall	Wafer	Bottom tube
Clean quartz (a.u.) Calibrated	0.61	4.42	0.52
Calculated (abs. ref.)	0.0077	0.056	0.0066
Calculated abs. ref. With GaAs deposit	0.043	0.185	0.002
Arbitrary scale (calculated for GaAs)	3.39	14.60	0.16

Table 3.5: Table of the calibrated arbitrary units of reflection, with calculated absolute reflectance for a clean quartz surface, and for quartz with a GaAs deposit. Also shown is the calculated equivalent reflection using the arbitrary scale for when a GaAs deposit is present.

When the deposited GaAs was rough, reflection from the top of the tube may have been scattered, which would be the case for reflection from the bottom of the tube as soon as GaAs was deposited. In this case, detected laser reflection may have only been from the deposit on the quartz slide.

3.3 Analytical techniques

After each experimental run, the deposit was analysed using several analytical techniques. The surface techniques that were employed included:

- X-ray diffraction (XRD), which gave information on the orientations present in the polycrystalline GaAs material.
- Scanning electron microscopy (SEM) and atomic force microscopy (AFM) which gave topographical information. The surface morphology of each sample was expected to compliment the reflectance data, where increased surface roughness increased reflectance scattering, reducing the reflectance intensity detected.
- Inductively coupled plasma atomic emission spectroscopy (ICP-AES), which gave quantitative measurement of the Ga and As composition in the whole of the parasitic deposit.

3.3.1 X-ray diffraction

The incident beam in XRD uses an electrically heated filament, usually tungsten, which emits electrons which are accelerated towards an anode using a high potential difference (20 - 50 kV). The anode (which is water cooled) emits a continuous spectrum of white radiation. In addition to this, the bombarding electrons knock out electrons from the inner most K shell of the anode atoms. Electrons then descend from shells above to fill the vacancies from the L and M shells. Copper is commonly used as the target metal (anode), and its emission spectrum has K_{α} (electrons from L shell) and K_{β} (electrons

from M shell) peaks superimposed on a broad peak due to the Bremsstrahlung radiation. The copper becomes ionized with the electron bombardment and the K lines shift to shorter wavelengths. Monochromatic radiation is generally used in XRD, with the K_{α} line being selected. The K_{β} line is filtered out by using nickel filters for copper anodes, which is the adjacent element on the periodic table. The monochromatic beam may also be selected by reflecting the beam from a single crystal, such as graphite.

X-ray diffraction occurs when the incident wavelength is the same order of magnitude as the spacing of the crystal being probed. The X-rays reflect from the planes of the crystal structure at specific orientations of the sample. The angle of incidence equals the angle of reflection and is possible for all angles where there is constructive interference. This was first noticed by W.L. Bragg in the early 1900s. For constructive interference to occur, the path lengths of the interfering beams must differ by an integral (n) number of wavelengths (λ). Figure 3.12 is a diagram illustrating Bragg reflection from a set of crystal planes with a spacing d_{hkl}.



Figure 3.12: Bragg reflection from a set of crystal planes with spacing d_{hkl} [3.4].

The difference in path length is expressed in the Bragg equation:

 $n\lambda = 2d_{hkl}\sin\theta_{hkl}$.

(3.26)

A peak list for GaAs x-ray diffraction with copper K α radiation is shown in Table 3.6, which was obtained from the International Centre for Diffraction Data (ICDD).

No.	h	k	1	d (Å)	2θ (deg)	Rel. I (%)
1	1	1	1	3.26300	27.31	100.0
2	2	0	0	2.82500	31.65	1.0
3	2	2	0	1.99820	45.35	50.0
4	3	1	1	1.70460	53.73	38.0
5	2	2	2	1.63190	56.33	1.0
6	4	0	0	1.41360	66.04	8.0
7	3	3	1	1.29720	72.86	10.0
8	4	2	0	1.26430	75.07	1.0
9	4	2	2	1.15400	83.75	9.0
10	5	1	1	1.08810	90.13	6.0
11	4	4	0	0.99940	100.85	5.0
12	5	3	1	0.95550	107.45	5.0
13	6	2	0	0.89390	119.02	3.0
14	5	3	3	0.86220	126.61	2.0
15	4	4	4	0.81610	141.43	1.0

Table 3.6: Peak list of a GaAs sample, reference number 00-032-0389, from a powder diffraction file (PDF-2) supplied by the ICDD [3.5].

At low temperatures, the parasitic deposit in the Aixtron reactors was reported [3.6] to consist mainly of arsenic. It is possible that the crystal structure of arsenic would also be observed in the XRD data, as the main structure of the deposit, or in a mixed phase crystal structure with that of GaAs. Below is a Table showing the peak list of an arsenic sample for a reference material from the powder diffraction file also supplied by the ICDD. The crystal structure was rhombohedral (trigonal), which is the most common crystal structure of arsenic. The crystal structure for arsenic can also be orthorhombic or tetragonal. In the MOVPE process, arsenic may form as As₂ or As₄, the latter being more stable [3.7]. Therefore, Table 3.7 represents XRD data for a sample with a rhombohedral crystal structure.

No.	h	k	1	d (Å)	2θ (deg)	Rel. I (%)
1	0	0	3	3.52	25.31	13.2
2	1	0	1	3.11	28.67	3.2
3	0	1	2	2.77	32.29	100.0
4	1	0	4	2.05	44.16	27.4
5	1	1	0	1.88	48.38	28.2
6	0	1	5	1.77	51.58	9.7
7	0	0	6	1.76	51.98	3.2
8	1	1	3	1.66	55.38	5.9
9	0	2	1	1.61	57.21	0.3
10	2	0	2	1.56	59.36	12.0
11	0	2	4	1.39	67.57	5.5
12	1	0	7	1.37	68.57	5.3
13	2	0	5	1.29	73.41	2.5
14	1	1	6	1.28	73.73	4.9

Table 3.7: Peak list of an As sample with a rhombohedral crystal system, reference number 01-072-1048, from a powder diffraction file (PDF-2) supplied by the ICDD [3.5].

3.3.2 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Electrons are used to probe the sample surface in SEM, which cause a number of interactions with the atoms in the sample material when they hit the surface, while some electrons may be backscattered if the electrons collide with atoms at near normal incidence. The electrons that probe the surface are produced in an electron gun consisting of a tungsten filament, which is heated by passing a current through it while being held at a high negative potential in comparison to an anode and the rest of the microscope positioned below the filament.

The anode has a hole at the centre, and electrons from the filament are accelerated through it into the microscope column under high vacuum. Control of the electron beam diameter is achieved by using a Wehnelt cap, positioned just below the filament, which is slightly more negative than the filament. The path of the electrons crossover at a point in space once leaving the anode, the point of crossover reflects the size of electron source and determines the resolution of the microscope. The difference in potential between the Wehnelt cap and the tungsten filament controls the beam diameter at the

crossover point as it is dependent on the area of the filament where electrons are emitted. Figure 3.13 is a schematic of the SEM equipment.



Figure 3.13: Set-up of the SEM with sample and stimulated emission.

A condenser reduces the diameter of the electron beam until it reaches 5 - 10 nm at the surface of the sample. Deflector coils scan the electron beam across the sample and a detector counts low energy secondary electrons given off from each point on the surface. Secondary electrons are produced by the electrons in the incident beam passing near to an atom in the sample giving some of their energy to other electrons. The incident beam changes path direction, while the electron in the sample is ionised leaving the atom with small kinetic energy (5 eV). Only secondary electrons close to the surface of the sample (<10 nm) are able to leave the sample where they are detected with the aid of a collector, which has a grid with +100 V potential applied to it placed in front of the detector. Secondary electrons are attracted towards the grid and pass through the holes before being counted by the detector. A spot of the electron beam is scanned across a cathoderay tube at the same time the sample is scanned. The brightness of the image is controlled by the number of secondary electrons counted by the detector, producing a magnified image on the cathode-ray tube.

In EDX, the emitted X-rays from the sample are utilised for analysing the surface. Electrons from atoms within the sample may fall from a higher energy state into a space left by an emitted secondary electron. This causes the atom transition from a high energy state to a lower energy state, releasing some of its energy. X-rays are emitted, in the same way X-rays are emitted from the copper anode in XRD, the different energies and wavelength of each emitted X-ray being specific to each elemental atom at the surface of the sample. The X-rays are measured by a detector placed close to the sample, which is cooled by liquid N₂ to minimise noise effects. Electrons within the detector are excited to the conduction band by the X-rays, leaving an equal number of positively charged holes in the outer electron shells. The energy of the X-ray being absorbed is proportional to the number of generated electron-hole pairs. The application of voltage across the detector produces a current for each X-ray absorbed, with magnitude exactly proportional to the energy of each X-ray. The produced current pulses are amplified and then passed to a multi-channel analyser recording a histogram of the X-ray energies characteristic to the elements from which X-rays were emitted. Figure 3.14 is a typical histogram recorded from EDX of an AlGaAs deposit on a quartz top plate of an Aix-2400 multi-wafer reactor. The sample was supplied by IQE.



Figure 3.14: EDX Scan of an AlGaAs deposit on a fragment of a quartz top plate of an Aix-2400 commercial reactor.

Table 3.8 is the peak list of elements detected.

Label	Range (eV)	Gross	Net	%Total
C (Κα)	0.188 to 0.368	5627	1957	14.2
Ο (Κα)	0.428 to 0.627	7463	3322	24.2
Ga (L α_1)	0.988 to 1.148	13218	2621	19.1
As $(L\alpha_1)$	1.168 to 1.388	14363	2351	17.1
Si (Ka)	1.628 to 1.847	4011	1455	10.6
Cl (Ka)	2.507 to 2.747	2007	311	2.3
Ga (Ka)	9.068 to 9.427	1924	1316	9.6
As (Ka)	10.347 to 10.727	1033	403	2.9

Table 3.8: EDX peak list of the AlGaAs deposit on a fragment of quartz top plate of an Aix-2400 commercial reactor.

The sample has chlorine (Cl) present due to the sample being etched with hydrochloric acid (HCl) after the process run within the commercial reactor. Carbon (C) is present due to its incorporation from decomposition of the organometallic precursors (Ga- and Al-containing compounds). When the deposit was exposed to air, oxidation of the deposit occurred over time resulting in detectable amounts of oxygen (O) recorded in the EDX histogram. The K α emissions were a result of an electron transition from the L shell to the K shell of the elemental atom, and L α_1 from an electron transmission from the M shell to the L shell of the elemental atom.

3.3.3 Atomic force microscopy (AFM)

The surface of the sample is scanned using a tip on the end of a cantilever which bends in response to the intermolecular force between the tip and the sample. A laser is directed towards the top of the cantilever above the tip and is reflected onto a split photodiode. The cantilever flexes as the tip scans over the surface of the sample as in Figure 3.15, which changes the angle of laser reflection detected by the split photodiode measuring the difference signal.



Figure 3.15: Surface probe of the AFM.

Small displacements caused by the flex of the cantilever enables the interaction force between the tip and the sample to be calculated using Hooke's law. A positioning device, usually a tube scanner, allows precise movement of the tip and can achieve resolution smaller than Angstroms (Å) in the x-, y- and z-directions. Operation of the AFM may use feedback control. This allows the tube scanner that is moving the tip (or sample) up and down to respond to any changes in the force that is detected, altering the tip-sample separation to restore the force to a pre-determined value. This is known as constant force operation.

Without feedback control, the microscope operates in deflection mode, generally used for very flat samples at high resolution. Thermal drift or the possibility of a rough sample damaging the tip may be avoided by using a small amount of feedback-loop gain, which gives an additional error signal. The error signal mode may also be used with feedback control, removing slow variations in the topography image, highlighting edges of features. When the sample and tip remain in close contact, an intermolecular repulsive force keeps them separated.

The cantilever may also be set in tapping mode, where it oscillates at a resonant frequency. Inter-molecular repulsion forces between the tip and sample prevent actual contact with each tap of the cantilever, which occurs for a small fraction of its oscillation period. Lateral forces present in the constant force method are removed due to the reduced time over which the tip scans the surface. Using constant force mode in combination with tapping mode, the amplitude of the cantilever oscillation is nearly

constant. Small changes in the oscillation amplitude occurs due to the control electronics not responding instantaneously to changes in the surface topography, allowing image contrast to be obtained.

3.3.4 Inductively coupled plasma – atomic emission spectroscopy (ICP-AES)

ICP-AES is another technique that detects emitted energy from excited electrons returning to the ground state. Each wavelength emitted is characteristic to a specific element. It is a quantitative technique where a sample containing known elements is analyzed. The sample is prepared as a solution and calibrated against a standard, which is a known concentration of the specific element being characterized.

The fluid sample is pumped into a nebulizer, which generates an aerosol mist that is injected with humidified argon (Ar) gas into a chamber. The mist accumulates in a spray chamber with larger particles settling out as waste. Only the finest particles are utilized, which are transported into a heated area known as the torch. A plasma consisting of Ar ions is generated at a temperature around 10 000K. The detector is fixed at the end of the spectrometer. Emitted wavelengths are detected separately using a diffraction grating. The intensity at the detector at any given time is correlated with the wavelength being diffracted by the grating. The target wavelengths are inputted using a computer and the grating sequentially moves to the specified wavelength. The intensity at each wavelength is measured to obtain a quantitative result to be compared to the reference standard.

The samples were prepared by dissolving the whole tube deposit, and wafer deposit from each experiment into aqua regia. This consisted of a 3:1 mixture of concentrated hydrochloric acid (HCl) to concentrated nitric acid (HNO₃). The wafer deposit was prepared separately to the tube deposit, as another wafer was positioned at the end of the heated zone. A comparison to the central wafer deposit would show any differences in composition as a result of gas phase depletion towards the exhaust. It was envisaged

that this would give insight into dominant reaction pathways in the process, which would more likely occur at the central wafer relative to the exhaust wafer.

3.4 Theoretical model

A model was developed from kinetic parameters (Chapter **2.4.2**) published in the literature [3.8, 3.9, 3.10, 3.11] for gas phase and surface reaction mechanisms. The temperature range used in the calculations reflected the experimental temperature, which was in the kinetic-limited regime for GaAs deposition where surface reactions limit the deposition rate. The reactions were assumed to be first order with respect to the AsH₃ over-pressure used in the experimentation. The data from Table 2.1 (page 52) and 2.2 (page 55) are parameters that make up the Arrhenius equation:

$$\mathbf{k} = \mathbf{A} \cdot \exp^{\left(\frac{-E_a}{\mathbf{RT}}\right)}.$$
(3.27)

The rate constant, k (cm³ mol⁻¹ s⁻¹), is expressed by the pre-exponential (or frequency) factor, A (cm³ mol⁻¹ s⁻¹), activation energy E_a (J mol⁻¹), gas constant, R (J K⁻¹ mol⁻¹), and temperature, T (K). The effect of temperature and activation energy affected each reaction mechanism to a different degree. Therefore, some reaction pathways dominated at a lower temperature, whilst other reaction pathways became more dominant with an increase in temperature changing the deposition process, and resulting in a different degree temperature used in the experimentation, rate constants were calculated for each reaction mechanism. Initial concentration was calculated using the method in Section **3.1.1** for TMGa, AsH₃ and H₂ as the gases entered the reactor chamber where the precursor decomposed and reacted. Partial pressures were calculated for the precursor and carrier gas species using the method in Section **3.1.1**. These parameters were then utilised in the steady state approximation to obtain expressions for product species from the decomposition of the parent species TMGa and AsH₃.

3.4.1 Steady state approximation (SSA)

The SSA assumed that intermediate species concentrations were constant. Figure 3.16 is a flow diagram of all the reaction pathways used in the model involved in the GaAs deposition process.



Figure 3.16: Flow mechanism of the reaction pathways involved in GaAs deposition during MOCVD.

The reaction routes shown with black arrows were considered the dominant pathways and their kinetic parameters were used for quantitative calculation of product yield for the major growth species MMGa(s), AsH(s), Ga(s), As(s) and GaAs. The reaction mechanisms with blue arrows were excluded from the model also for reasons discussed in Chapter 4, where the results are also presented and discussed. An example of how the

SSA was used, starting from initial reactions of the precursors TMGa and AsH_3 and the H_2 carrier gas is shown below.

k	Reaction step
k _{S10}	$Ga(CH_3)_3 + s_{As} \rightarrow GaCH_3(s_{As}) + 2(^{\bullet}CH_3)$
k _{G15}	$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3$
k _{G4}	$H_2 + CH_3 \rightarrow CH_4 + H^{-1}$
k _{G5}	$Ga(CH_3)_3 + CH_3 \rightarrow Ga(CH_3)_2CH_2 + CH_4$
k _{G13}	$Ga(CH_3)_3 + H^* \rightarrow Ga(CH_3)_2 + CH_4$
k _{S1}	$H^{\cdot} + s (s_{As} \text{ or } s_{Ga}) \rightarrow H(s)$
k _{G19}	$AsH_3 + CH_3 \rightarrow AsH_2 + CH_4$
k _{G20}	$AsH_3 + H^* \rightarrow AsH_2 + H_2$

Table 3.9: Reaction mechanisms involved in initial decomposition of the precursors.

From the reaction mechanisms above the concentrations of the intermediate species can be represented using the SSA. The concentrations of radicals H^{\cdot} and ${}^{\cdot}CH_3$ are represented below for initial reactions involved in the process. The mathematical relationship changed as the reaction pathways progressed towards the deposition of GaAs at the surface.

Rate of change for $[\cdot CH_3] = 0$ by SSA:

$$\frac{d[CH_3]}{dt} = 2k_{s10}[TMGa] - k_{G4}[\cdot CH_3][H_2] - k_{G5}[TMGa][\cdot CH_3] - k_{G20}[AsH_3][\cdot CH_3] + k_{G15}[TMGa] - k_{S2}[\cdot CH_3] = 0.$$
(3.28)

$$[\cdot CH_{3}] = \frac{2k_{S10}[TMGa] + k_{G15}[TMGa]}{k_{G4}[H_{2}] + k_{G5}[TMGa] + k_{G20}[AsH_{3}] + k_{S2}}.$$
(3.29)

Rate of change for [H·]:

$$\frac{d[\mathbf{H}\cdot]}{dt} = k_{G4}[CH_3][H_2] - k_{G13}[TMGa][\mathbf{H}\cdot] - k_{G19}[AsH_3][\mathbf{H}\cdot] - k_{S1}[\mathbf{H}\cdot] = 0.$$
(3.30)

$$[\text{H}\cdot] = \frac{k_{\text{G4}}[\text{CH}_3][\text{H}_2]}{k_{\text{G13}}[\text{TMGa}] + k_{\text{G19}}[\text{AsH}_3] + k_{\text{S1}}}.$$
(3.31)

Using initial concentrations for TMGa, AsH₃ and H₂, the concentration of CH_3 was expressed as in Equation (3.29) using the first few steps involved in the reaction mechanism. A relationship for [H·] was then expressed as in Equation (3.31) by substituting [CH_3] with the expression in Equation (3.29). This method was followed for progressive steps, resulting in expressions for [species] for each mechanism in the reaction pathway. As the reaction steps became more complex, iteration was applied to the expressions representing each reaction step until a constant value was obtained for each species concentration. Progressive steps were then added to the expressions for each species following the same method. The surface species involved in GaAs formation were represented in the equations shown in Appendix 2. Their concentration at the surface was dependent upon the sticking coefficient, represented by θ (Equation 3.32).

$$\theta = \frac{\sqrt{\left(\frac{k_{ads}}{k_{des}}\right) \times p_{species}}}{1 + \sqrt{\left(\frac{k_{ads}}{k_{des}}\right) \times p_{species}}}$$
(3.32)

The rate constant for adsorption and desorption are represented by k_{ads} and k_{des} respectively, and $p_{species}$ is the partial pressure of the reacting species. With the metal atoms and partially decomposed species adsorbed at the surface, and their subsequent reaction with one another, GaAs may be produced. The following expression represents the rate of GaAs forming at the surface:

$$R_{[GaAs]} = k_{s33}[Ga(s)][As(s)] + k_{s34}[MMGa(s)][AsH(s)] + k_{s35}[MMGa(s)][As(s)]$$
(3.33)

The rate expression for GaAs was used in Equations 3.34 and 3.35 to calculate the product yield in the deposit. The method to calculate the yield (mg) for GaAs is shown below:

$$n_{GaAs} = t \cdot F_{tot} \cdot R_{GaAs} \tau$$
(3.34)

$$m_{GaAs} = n_{GaAs} \cdot mol.wt_{GaAs}$$
(3.35)

The value of time, t (s), was 3600 s, F_{tot} is the total flow (cm³ s⁻¹), R is the rate (mol. cm⁻³ s⁻¹), τ is the residence time (s), m is the mass of the species (mg) and the molecular weight (mol. wt.) was in mg mol⁻¹. The concentrations for the 4 reacting surface species to form GaAs were calculated for the different V/III ratios 10, 30 and 50, where p_{AsH_3} was kept constant and p_{TMGa} varied. The results are shown in Chapter 4 and an example of a method used for one of the V/III ratios is shown in Appendix 1.

3.5 References

- [3.1] T. Bergunde, F. Durst, L. Kadinski, Yu.N. Makarov, M. Schafer, M. Weyers; J. Crystal Growth 145 (1994) 630.
- [3.2] T. Bergunde, M. Dauelsberg, L. Kadinski, Yu.N. Makarov, M. Weyers, D. Schmitz, G. Strauch, H. Jurgensen; J. Crystal Growth 170, (1997) 66.
- [3.3] K.J. Weeks, S.J.C. Irvine, S. Bland, J. Crystal Growth 257 (2003) 116.
- [3.4] "Solid State Chemistry, An instruction", L. Smart, E. Moore, Chapman and Hall, 2nd Edition (1995) 83.
- [3.5] P. Gong, Polytechnic Inst of Brooklyn, NY, USA., ICDD Grant-in-Aid, (1981).
- [3.6] T. Bergunde, D. Gutsche, L. Kadinski, Yu. Makarov, M. Weyers; J. Crystal Growth 146, (1995) 564.
- [3.7] "Organometallic Vapour-Phase Epitaxy: Practice and Theory", G.B. Stringfellow, Academic Press, 2nd Edition (1999).
- [3.8] T.J. Mountziaris, K.F. Jensen, J. Electrochem. Soc. 138, (1991) 2426.
- [3.9] M. Tirtowidjojo, R. Pollard, J. Crystal Growth 93, (1988) 108.
- [3.10] S. Mazumber, S.A. Lowry, J. Crystal Growth 224, (2001) 165.
- [3.11] "Handbook of Crystal Growth", D.T.J. Hurle, Elsevier, (1994) 459.

4.0 Results and discussion

4.1 Experimental results

Presented and discussed in this section is the *in situ* reflectance data from various experiments where temperature ranged from 400°C to 500°C, and the V/III ratio was either equal to 10, 30 or 50, keeping p_{AsH_3} at 0.85 mbar. The results from analysis of each deposit on the quartz slide placed inside the reactor tube for each experiment are also presented and discussed.

4.1.1 Reflectance data produced from deposition experiments

Figure 4.1 represents an interferogram obtained from an experiment before calibration of the laser diode had been carried out. The intensity of the laser diode was greater than that for the experiments carried out after calibration (Figure 3.8, page 75). After calibration, the intensity was kept constant afterwards to allow comparison of reflectance from the three different points of reflection inline with the laser.



Figure 4.1: Interferogram of run carried out at 475°C, V/III = 30.

The reflection intensity in Figure 4.1 when GaAs was deposited was much greater than for a clean quartz surface resulting in the large intensity reading. When the GaAs was deposited onto the quartz surface, the reflection intensity became saturated. Saturation was observed to occur when the intensity reading was ≥ 10 a.u. over a period of time, which was the maximum intensity on the arbitrary scale. The saturation of the intensity signal hides a lot of growth rate information and so was not useful for interpretation. Decreasing the laser intensity resulted in a reduced difference in reflected intensity between the quartz and GaAs surface. This was done to prevent saturation occurring for other experiments and the reflectance intensity was calibrated.

With larger intensity of the laser incidence, more of the reflected beam was detected. The intensity of transmittance is also higher. The percentage of the beam reaching the detector is the same whatever the laser intensity. When GaAs was deposited onto the quartz slide, the intensity difference between detected reflection from GaAs and quartz increased with the intensity of the laser incidence. This is illustrated in Figure 4.2. More of the laser beam was able to penetrate the top wall deposit and reflect as observed in Figure 4.1, where reflectance intensity from the GaAs surface was much larger than for the clean quartz slide.



Figure 4.2: Change in reflectance intensity from quartz and GaAs when the laser diode intensity is reduced by 50%.

Oscillations were not always observed during growth. The general trend for the reflectance data obtained was a decrease in signal once nucleation initiated, followed by recovery of the signal. Without the presence of oscillations the reflectance signal generally decreased during deposition until the signal recovered slightly where the reflectance intensity stabilised. Below are two examples of reflection data obtained at 500° C, Figure 4.3 was with V/III = 10 and Figure 4.4 was with V/III = 50.



Figure 4.3: Interferogram of run carried out at 500°C, V/III = 10.



Figure 4.4: Interferogram of run carried out at 500°C, V/III = 50.

The difference between Figure 4.3 and 4.4 is that the latter interferogram had oscillations due to layered growth of GaAs on the quartz slide whilst the other did not. Both experiments were carried out at the same temperature, but p_{TMGa} was 0.017 mbar in the experiment represented by Figure 4.4 whereas the in the other experiment p_{TMGa} was 0.085 mbar. Both interferograms resulted in a reflected intensity around 3 a.u. where an average reflection from the deposit was recorded. The reflection intensity in both interferograms reduced initially, which was most likely due to 3-dimensional growth on the quartz.

From Figure 4.3 it appears that the deposition of GaAs with p_{TMGa} at 0.085 mbar occurred with a slightly different mechanism, where growth was always rough with irregular coalescence of the growth islands. With more surface Ga-species likely at this temperature, the rate of deposition would have been greater than at the lower temperatures towards 400°C. It was possible that the 3-dimensional growth proceeded at a greater rate than coalescence was able to occur. Partial recovery of reflectance intensity was probably due to complete surface coverage of the slide while 3-dimensional growth continued to increase and coalesce over time.

With the experiment where p_{TMGa} was equal to 0.017 mbar, represented in Figure 4.4, the laser incidence beam was increasingly absorbed over time indicated by the reduction in amplitude of the oscillations. Both interferograms have initial oscillation(s) during the decrease in reflection intensity in the early stages of growth. It is proposed that this was due to changes in reflection from the top of the quartz tube deposit, where the surface area being probed was curved, where coalescence of the 3-dimensional islands occurred sooner. This could be because of a slightly higher temperature at the top of the quartz wall as well as due to the curvature of the wall. After coalescence, it was likely that further deposition at the wall was 3-dimensional and continued to be rough over time. Oscillations were only observed from 450°C to 500°C. At 425°C the growth rate was too slow to enable one complete oscillation to occur. Table 4.1 represents the conditions when oscillations were observed in the reflectance data.

V/III ratio

450°C :	10	30	
475°C:	10	30	
500°C:		30	50

Table 4.1: Temperature and V/III ratio conditions used in experiments when oscillations were observed, $p_{AsH_3} = 0.85$ mbar, $p_{TMGa} = 0.085$ mbar (V/III = 10), 0.028 mbar (30), 0.017 mbar (50).

There appears to be some sort of trend where oscillations were observed when both temperature and V/III ratio were low, or both were high. An over-pressure of AsH_3 was used in all experiments, which was to eliminate effects of AsH_3 desorption. The input concentration and the level of AsH_3 desorption were considered to be factors towards whether 2-dimensional growth occurred. The reflectance data was dependent on 2-dimensional growth where oscillations were observed.

At 450°C and 475°C, no oscillations were observed when a V/III ratio of 50 was used, which was the largest over-pressure of AsH_3 employed in experiments. It was expected that the concentration of Ga-species at the surface was not large enough with respect to the large AsH_3 over-pressure. The surface was most likely covered by As-species. Increasing p_{TMGa} (V/III ratios 30 and 10) would have increased the concentration of Ga-species at the surface reaction to form GaAs where coalescence and 2-dimensional growth was more probable.

At 500°C, oscillations were observed when a V/III ratio of 50 was used, whereas oscillations were not observed using a V/III ratio of 10. This was considered to be because desorption of As-species was more prominent at this temperature, which compensated for the lower concentration of Ga-species at the surface. It was determined that 2-dimensional growth was more likely when the conditions favoured GaAs formation at the surface. Concentration of the Ga- and As-species would not have to have been stoichiometric, but deviation from this could not be too large where deposition would be more 3-dimensional.
Figure 4.5 shows an interferogram from an experiment carried out with V/III equal to 10. The experiment was carried out at a slightly lower temperature than the experiments where oscillations were observed for the higher V/III ratios. In this case, surface reactions involving Ga-species would have been slower.



Figure 4.5: Interferogram of run carried out at 450°C, V/III = 10.

At lower temperatures, desorption of As-species was expected to be less prominent. So even at lower V/III ratios where surface concentration of Ga-species was high, the rate of surface reaction of Ga-species would be slow. The reaction to form polycrystalline GaAs was considered to be more likely than a deposit consisting mainly of Ga-species. At higher p_{TMGa} and with an increase in temperature, Ga-species would have deposited at the surface more rapidly, whereas more As-species would have desorbed. The decrease in surface reaction of Ga-species, where surface saturation was considered likely with large p_{TMGa} , was expected to lead to a GaAs deposit. This would be more 2dimensional, where As deposition was reduced due to a reduction in temperature, with the surface reaction rate of Ga-species controlling the growth. Therefore, with high p_{TMGa} at lower temperatures (Figure 4.5) oscillations are more likely to be observed in the reflectance signal due to polycrystalline GaAs growing layer by layer at the surface.

Elevating the temperature increases the surface reaction rate, thus a larger input of precursor is required for saturation to be reached. At higher temperatures, desorption of As-species becomes more prominent, and compensation for this was achieved by reducing the supply of TMGa for polycrystalline GaAs to be deposited rather than Ga droplets. Here the reduced concentration of Ga-species at the surface and the adsorption/desorption rate of As-species would control the growth rate. The relationship between temperature and supply of TMGa and the effect on growth rate is represented by Figure 4.6. There are no data points for growth rate between p_{TMGa} at 0.028 and 0.085 mbar representing V/III ratios 30 and 10. However, the growth rate can be seen to have increased with p_{TMGa} and temperature, with less difference of growth rate values between 0.028 and 0.085 mbar than between 0.017 and 0.028 mbar. The surface was therefore saturated with Ga-species at p_{TMGa} not much higher than 0.028 mbar (V/III of 30). It is evident that with an increase in temperature, this surface saturation required a higher p_{TMGa} due to increased surface reactions of the Ga-species.



Figure 4.6: Observed temperature and V/III ratio effects on nucleation and deposition rate.

The reflectance intensity obtained from the walls of the quartz tube and from the quartz wafer without a deposit were measured as presented in Figure 3.8 (page 75) and converted to absolute reflectance using Equation 3.19 (page 76). The absolute reflection was then calculated considering the presence of a GaAs deposit using Equations 3.20 and 3.20 (page 76) as well. Total absolute reflectance is equal to 1.0, and was calculated to be equivalent to 78.93 (a.u.) on the arbitrary scale of the laser reflectance intensity from the top tube wall should have been 5.05 (a.u.), whereas 0.61 (a.u.) was detected. It was expected that most of the laser was reflected at an angle to that of the incidence probe due to the curvature of the tube. A similar outcome was observed from the bottom tube wall. The reflectance was calculated assuming that 100% of the reflection was being detected from the quartz slide, where the surface was flat.

The calculated absolute reflectance for the quartz tube walls and quartz wafer considering the presence of a GaAs deposit were transferred to the arbitrary scale used in experiments. The presence of a 2-dimensional film on the reactor walls would increase the reflectance from the curved surface, reducing the amount of reflection reaching the detector. The model did not take this into account, nevertheless, the expected reflectance intensity from the model, including reduced reflectance from the quartz tube due to its curvature, and assuming 2-dimensional growth of GaAs was calculated to be;

Top of quartz tube with GaAs - 3.39 (a.u.); Quartz slide with GaAs - 14.60 (a.u.); Bottom of quartz tube with GaAs - 0.16 (a.u.).

This, however, does not correlate to that observed in the reflectance data presented earlier in this Chapter. This was determined to be due to 3-dimensional island growth of the GaAs (or related species) deposit, which is discussed in more detail in the following Section. With 3-dimensional growth taken into consideration, the detected reflection from the bottom wall of the reactor tube was neglected. Had 2-dimensional growth of GaAs been occurring, one would have expected to have observed saturation of the reflection intensity as the arbitrary scale used in the reflectance measurements only went to 10 (a.u.). The observed reflection intensity from the three points of reflection inline with the incident beam, calculated from Equations 3.19 - 3.21 (page 76), would have been 19.24 (a.u.) on the arbitrary scale. Saturation was observed during one experiment after calibration, represented in Figure 4.7, where Ga had deposited initially without the presence of As-species.



Figure 4.7: Interferogram from experiment carried out at 450°C, V/III = 30. TMGa was introduced into the reactor chamber without AsH_3 for the first 15 minutes before AsH_3 was included.

TMGa was introduced solely for the first 15 minutes. Deposition of a Ga-species was observed from the change in reflection signal of the incident beam. A sharp transition occurred coinciding with the addition of AsH₃. There was a sharp loss of signal as Asspecies also deposited at the surface. This was attributed to a composition change at the surface from Ga to GaAs. The sharp increase in intensity was a result of GaAs growth, GaAs being more reflective than Ga. This was expected to be occurring at the quartz wafer positioned at the centre of the reactor tube due to the large reflectance signal. The point at which the reflectance saturated was calculated using the absolute reflectance model. It was determined that this intensity would have been 14.60 (a.u.), corresponding to a temporary 2-dimensional GaAs film at the quartz wafer during

conversion of Ga to GaAs. Subsequent deposition with both Ga- and As-species at the surface increased surface roughness of the growing deposit, where reflection intensity was observed to decrease over time.

The absolute reflection model may be of more use for epitaxial deposition of thin films deposited on substrates, where growth can be expected to be more uniform. It has given insight into the amount of laser reflection that can be scattered by the curvature of a reflecting surface and by the 3-dimensional island growth of the deposit during deposition. This helps to identify where the reflections are coming from in a multi-surface system and correctly attribute growth rate and thickness. Analysis of the surface morphology shows that even when oscillations were observed, 3-dimensional growth accompanied the layered growth. This reduced the reflectance intensity expected from the calculation in the absolute reflectance model.

Similar experiments to that represented in Figure 4.7 were carried out at 475°C and 500°C. The reflectance data for the latter temperature is shown in Figure 4.8.



Figure 4.8: Interferogram from experiment carried out at 500°C, V/III = 30. TMGa was introduced into the reactor chamber without AsH_3 for the first 15 minutes before AsH_3 was included.

As Ga-species adsorbed to the surface (109 seconds), the reflectance intensity was observed to decrease until reaching stable reflectance intensity. The addition of AsH_3 then decreased the reflectance intensity further due to island growth, before partial recovery of the signal occurred. It is expected that at these temperatures no 2-dimensional layer conversion from Ga to GaAs occurred, as the initial Ga deposit was too thick.

Figure 4.9 represents a similar experiment to the one shown in Figure 4.7, but this time AsH_3 was introduced on its own into the reactor chamber initially. It can be seen that there is no change in signal, which was expected as AsH_3 in H_2 is reported [4.1, 4.2] not to decompose until temperatures around 650°C. With the addition of TMGa, the signal decreased due to both Ga- and As-species adsorbing at the surface, which was due to 3-dimensional growth on the quartz surface scattering the incident beam. As the film became smoother the signal recovered, but the surface was expected to be rough as the signal only partially recovered.



Figure 4.9: Interferogram from experiment carried out at 450° C, V/III = 30. AsH₃ was introduced into the reactor chamber without TMGa for the first 15 minutes before TMGa was included.

No significant growth was observed at 400°C or below in the experiments of this research, each run was started using a clean reactor tube. Therefore nucleation had to be established before deposition could become stable. Without the presence of existing wall deposits of polycrystalline GaAs, or deposited Ga-species, the temperature was too low for deposition to be observed. No arsenic deposit was observed at the lower temperatures in contrast to observations by Bergunde *et al.* [4.3]. It was expected that in their system As deposition was due to the hot gas phase species meeting a cooled ceiling, where condensation of the As-species was the dominant process and complex reaction mechanisms were less likely to be significant.

The temperature conditions in this study can be considered to be different for the gas phase as in the commercial set-up. This is because there was a temperature gradient within the Aixtron reactor, pronounced by the cooling gas above the quartz top plate. The quartz tube used in this study was surrounded by the heater element of the furnace, which maintained a constant temperature along the cross section of the tube. It was expected that the temperature may have fallen towards the edge of the furnace, which was represented by the absence of the deposit observed where the heated zone ended. Condensation was expected to occur beyond the furnace where the cooling coil was positioned.

4.1.3 Surface morphology of deposit grown under different conditions

Images of five samples were obtained using an optical microscope from experiments carried out at 425°C, 450°C and 500°C, with V/III of 50, and V/III ratios 10 and 30 carried out at 450°C. It was observed that there was no difference between images of samples deposited at different ratios, but a change in surface morphology was observed for samples deposited at different temperatures. Below are three images of the samples deposited at different temperatures and a V/III ratio of 50. Figure 4.10 is an image taken of a sample deposited at 425°C, using optical microscopy. It shows an irregular surface where surface coverage was expected to be incomplete. The areas with deposit are expected to be where the dark areas on the image are present.



Figure 4.10: Image (light field) of a sample deposited at 425° C and V/III = 50 using optical microscopy at 50x magnification.

The deposit was examined in more detail using SEM, Figure 4.11 is an image taken of the surface. It can be seen that growth was 3-dimensional, where some islands grew more rapidly than others, some producing nano-rod type structures at the surface. The quartz surface can be seen to be exposed, labelled in Figure 4.11, where adsorption of species had not occurred. This rough and varied 3-dimensional growth would have caused the decrease in recorded reflected intensity due to the increase in scattering.



Figure 4.11: SEM image (tilted 10°) of a sample deposited at 425°C and V/III = 50.

The deposit in Figure 4.11 could have been a result of oxide assisted growth, where SiO_x clusters (x>1) at the quartz surface aid nano-wire growth. Some of the Si atoms are bonded strongly to the quartz surface, which limits the cluster motion on the surface. Other highly reactive Si atoms are exposed to the vapour with their dangling bonds directed outward from the surface, which act as sites for the precursor species to bond to. The outer SiO₂ layer of the nano-wire stops diameter growth [4.4].

In III-V MOCVD (such as GaAs), the VS mechanism involves the continuous supply of the group III species to the substrate surface, where surface reactions are slow. The presence of group V species pushes the Ga into a mixed phase, creating a region that is supersaturated. This can result in precipitation of the group III species at the substrate interface and the nano-wire growth occurs. The sample in Figure 4.11 was from an experiment carried out at 425°C, where surface reactions would have been slow. The over-pressure of AsH₃ was high in comparison to other experiments. Thus, the concentration of Ga-species at the surface would not have been large, but it is possible that this built up due to the low surface reaction rates. At 450°C (Figure 4.12) the image of the deposit surface at 50x magnification with the optical microscope appeared to be smooth, with some white areas present which were thought to be pin holes in the deposit.



Figure 4.12: Image (light field) of a sample deposited at 450°C and V/III = 50 using optical microscopy at 50x magnification.

Figure 4.13 is an SEM image of a sample of the quartz slide from the same experiment. The surface can be seen to be rough, although there appears to be complete surface coverage. The image from the optical microscope did not have enough magnification to show the 3-dimensional growth on the quartz slide. In Figure 4.13 a large island can be observed which is placed on top of the surface extruding approximately 2-3 μ m above the rest of the deposit. It may be that the observed white areas in Figure 4.12 from the optical microscope image were due to such structures at the surface. This is confirmed by Figure 4.14 and 4.15 from a sample deposited at 500°C.



Figure 4.13: SEM image of a sample deposited at 450°C and V/III = 50.

Figure 4.14 is an image taken at 50x magnification using the optical microscope of a sample deposited at 500°C. It has white areas similar to Figure 4.12, which are larger in comparison and more widespread. When it is compared to the SEM image taken of a sample from the same quartz slide it is evident that the white areas are in fact due to 3-dimensional growth, which are in several groups on a smoother surface, and not the previously speculated pin holes.



Figure 4.14: Image (light field) of a sample deposited at 500°C and V/III = 50 using optical microscopy at 50x magnification.



Figure 4.15: SEM image (tilted 10°) of a sample deposited at 500°C and V/III = 50.

The SEM image shows advanced 3-dimensional growth which protrudes from a more 2dimensional layer, which occurs due to the rate of coalescence being greater than vertical 3-dimension growth. It could be that the areas where growth structures group together above the smoother surface were depositing at a greater rate as can be seen in Figure 4.11 from the experiment at 425°C, where some island structures were greater than others. The small island growth would coalesce to form a smoother deposit over time, but the rapid growth in certain areas could continue to occur over the same period of time leaving the groupings of 3-dimensional growth with greater vertical height.

Figure 4.16 shows an edge view of the same sample. It is clear that there is a 2dimensional layer with islands of growth protruding above the surface several microns high.



Figure 4.16: SEM image of a sample edge deposited at 500°C and V/III = 50.

Comparing Figure 4.16 with an SEM image of a sample from an experimental run at 475°C and V/III ratio also of 50 (Figure 4.17), islands (about 2.5 μ m in diameter) can also be seen on a smoother surface (about 2 μ m in thickness). The islands in the image at 475°C are less advanced than the ones present in Figure 4.16 (500°C), where the deposition rate would have been greater.



Figure 4.17: SEM image of a sample deposited at 475°C and V/III = 50.

The layer on the sample from the experiment carried out at higher temperature is observed to be thicker as a result of the larger growth rate. The presence of the 2-dimensional surface interfacing with the quartz surface in Figure 4.15 and Figure 4.16 correlates well with the reflectance data from Figure 4.4, where oscillations were observed. The layer can be seen to be thick for the same sample (about 5 μ m), which would absorb the laser during the later stages of deposition. The increasing areas of 3-dimensional growth would have increased scattering of the laser incidence beam. Also, the growth rate can be seen to have decreased over time in Figure 4.4. Thus it is possible that growth slowed significantly that the change in reflection intensity was not noticeable leading to the observed constant intensity reading of approximately 3 (a.u.).

EDX was carried out on the 5 samples that were examined under the optical microscope. In all cases Ga was the dominant element at the surface. The presence of Si only observed from analysis of the sample from the experiment carried out at 425°C. The samples from experiments carried out at higher temperatures did not have any Si counts from the EDX analysis, due to the deposit being thicker due to faster reaction rate. Figure 4.18 and Figure 4.19 are two EDX histograms of samples taken at 425°C and 450°C, with V/III ratio equal to 50. The respective peak lists are shown in Table 4.2 and 4.3.



Figure 4.18: EDX histogram of a sample from an experiment run at 425°C, V/III = 50.

Label	% total
Ο (Κα)	8.9
Ga (L α_1)	30.7
As $(L\alpha_1)$	17.3
Si (Ka)	35.7
Ga (Ka)	6.8
Ga (Kß)	-0.7
As (Ka)	1.4

Table 4.2: EDX peak list of a sample from an experiment run at 425°C, V/III = 50.



Figure 4.19: EDX histogram of a sample from an experiment run at 450°C, V/III = 50.

Label	% total	
Ο (Κα)	0.2	
Ga (L α_1)	66.8	
As $(L\alpha_1)$	17.6	
Ga (Ka)	12.9	
Ga (Kß)	0.0	
As (Ka)	2.5	

Table 4.3: EDX peak list of a sample from an experiment run at 450°C, V/III = 50

The results from the two samples were compared to EDX of a GaAs substrate, shown in Figure 4.20 and Table 4.4. The Ga and As counts were very similar to that of Figure 4.19 and Table 4.3. The larger ratio of Ga to As at the surface was considered to be due to the arrangement of the surface atoms, consisting mainly of Ga. The orientation (or

preferred orientation with respect to the polycrystalline samples) of the deposited layers would influence this.



Figure 4.20: EDX histogram of a GaAs substrate.

Label	% total
Ga (L α_1)	63.3
As $(L\alpha_1)$	23.3
Ga (Ka)	12.3
Ga (Kß)	-0.6
As (Ka)	1.7

Table 4.4: EDX peak list of a GaAs substrate

Due to the deposits often being very rough, most of the samples were not suitable for analysis by atomic force microscopy (AFM). AFM requires a depth range of less than 3 μ m maximum in either direction for the tip (up or down). It was evident from the SEM images that the 3-dimensional islands in most of the samples were several microns in height. Figure 4.21 is an example of the surface roughness of the parasitic deposits grown on quartz. The sample was from an experiment carried out at 475°C where large islands would have grown due to relatively large deposition rates with respect to the temperature range (400 - 500°C) used in experiments.



Figure 4.21: AFM image taken of a sample from an experiment carried out at 475°C, V/III ratio of 50.

AFM is a technique that is often applied when the deposited material needs to be smooth and uniform for device operation. In the case for this study, the AFM image illustrates that the parasitic growth is very rough.

4.1.4 Crystal orientation in deposit

X-ray diffraction (XRD) was carried out on each quartz slide to see what orientations were present in the polycrystalline deposit. Figure 4.22 shows diffraction peaks for five temperature conditions ranging from 400°C to 500°C, with a V/III ratio of 30. The GaAs deposits have the preferred orientation of (111) from 425°C until 475°C, this agrees well with work done by Imaizumi *et al.* [4.5]. The relative intensity of the (220) orientation increases with temperature until dominating at 500°C. There was little deposit at 400°C, small peaks from the (111) and (220) orientations can be observed, the low broad peak is due to the quartz slide. At 500°C, with V/III = 50, the preferred orientation was (220). At 475°C and 450°C the (111) orientation dominated, with (220) only half the relative intensity. No growth was observed at 400°C or 425°C. The preferred orientation for V/III = 10 was always (111). The presence of amorphous GaAs was not ruled out, but it was expected that polycrystalline GaAs dominated.



Figure 4.22: XRD patterns of samples deposited at V/III = 30 over temperatures 673 - 773 K.

The XRD data from each sample was also compared to reference XRD data for arsenic from the ICCP database. The crystal structure for arsenic is commonly rhombohedral (trigonal), but may also be tetragonal and orthorhombic. Each possible crystal structure for arsenic from the ICCP database was compared to the experimental XRD data. There were some 2 θ positions similar to that found in GaAs for some of the orientations. Overall, however, it was concluded that there was no correlation between the XRD data from the experiments and that for the crystal structures of arsenic from the database. The deposit on the quartz wafer was determined to consist only of GaAs, with no As crystal structure present, even at low temperature. The presence of an As deposit on the cooled top plate in the Aixtron reactor observed by Bergunde *et al.* [4.6] was expected to be a result of condensation.

4.1.5 Nucleation time and growth rate

The nucleation time for deposition increased with a decrease in temperature, as would be expected where surface reactions limit the growth rate. It can be seen in Figure 4.23 that nucleation time was not dependent upon V/III ratio. There was a large difference between 425° C and 450° C, from which point nucleation was considered to be fast. At the lower temperature, the nucleation time for the experiment carried out at V/III = 30 can be observed to be a lot quicker than the other two ratios. Other factors at the lower temperatures are thought to be more significant, such as scratches which may be present at the quartz surface that may act as nucleation sites.



Figure 4.23: Nucleation time for deposition over a temperature range 400 - 500°C measured from the change in reflectance intensity during *in situ* monitoring.

The growth rate during initial deposition was observed to be greater than during the rest of the growth for the majority of experiments, which correlates well with results of Weeks *et al.* [4.7]. After initial layers were deposited the growth rate usually stabilised, but in some cases, the growth rate was observed to gradually decrease. Once nucleation had been established, it was expected that the growth kinetics would be comparable to that of epitaxial deposition.

The average growth rate was observed to increase with temperature, as shown in Figure 4.24, which was due to the increased rate of surface reactions in this temperature range which appeared to be the limiting factor for the overall deposition rate. The effect of V/III ratio is also shown, where lower V/III ratio (greater p_{TMGa}) increased the deposition rate. This was observed to be more significant at higher temperatures with increased surface reaction rates. At lower temperatures, where surface reactions were slower, further increase of p_{TMGa} would have reached a point of saturation of Ga-species at the surface, where an additional supply of TMGa would have had no more effect on the deposition rate [4.8].

It was reported by Tirtowidjojo and Pollard [4.9] and Mountziaris and Jensen [4.8] that at higher temperatures the decomposition of TMGa and DMGa became more important. The increased decomposition of these species would increase the supply of methyl radicals (\cdot CH₃), which occurred when p_{TMGa} was increased. Figure 4.24 shows initial reactions that may occur, involving TMGa, AsH₃ and H₂. It illustrates the importance of \cdot CH₃ production, reaction with H₂ produces hydrogen radicals (H[•]), both \cdot CH₃ and H[•] may react with AsH₃ to produce AsH₂. Carbenes can form from the reaction of \cdot CH₃ with TMGa, DMGa and MMGa, but these were not expected [4.8] to affect the growth rate and can readily react with H[•] to form the methylated Ga-species.



Figure 4.24: Average growth rate at different deposition temperatures at V/III ratios 10, 30 and 50 calculated from recorded interferogram oscillations.

These results are in agreement with investigations carried out using IR analysis [4.1, 4.2] of the decomposition products from the reaction between TMGa and AsH₃. Deposition was reported only to have occurred to any significant extent at 425°C and above. The rate of decomposition of the precursors was determined [4.1, 4.2] by the amount of CH₄ detected using IR. It can be seen in Figure 4.24 that no growth rate data was obtained at 425°C for V/III equal to 50, where p_{TMGa} was lower relative to the other two V/III ratios. It was expected that a combination of low TMGa concentration and low rate of reaction

at the surface resulted in very little deposit forming at the surface. The reaction rate was most likely too low for oscillations to be observed in the reflectance data.

Growth rate data was not measured by Bergunde's group [4.10] at the quartz top plate of the Aixtron reactor. It was calculated by Bergunde *et al.* to be $0.4 \,\mu\text{m}\,\text{hr}^{-1}$ (0.11 nm s⁻¹) where maximum parasitic deposit was observed. This relates to the growth rate observed at temperatures between 475 and 500°C in experiments carried out in this investigation, where it was measured to be between 0.05 and 0.2 nm s⁻¹, depending upon the V/III ratio employed. The growth rate decreased at the top plate in the Aixtron reactor in the radial position towards the inlet and the exhaust, where the position at the top plate moved further away from the position of the heated susceptor. This reduced the level of heat transfer to the area of the top pate. The growth rate measured at the lower temperatures in this investigation were 0.018 nm s⁻¹, which is approximately the value calculated by Bergunde *et al.* [3.10] where minimal parasitic growth was observed in their experiments.

4.1.6 ICP analysis of the total deposit produced in experiments

The GaAs yield obtained from experiments over the temperature range between 400°C and 525°C, using a V/III ratio of 50, was obtained by dissolving the whole deposit from the reactor tube and quartz wafer in aqua regia, as described in Chapter 3 (page 90). The results were produced in mg L^{-1} and were converted to mg, which are displayed in Table 4.5.

Temp (°C)	400	425	450	475	500	525
Ga (mg)	0.046	3.60	15.68	28.39	75.96	80.70
As (mg)	0.342	4.45	18.80	37.57	101.20	106.00
GaAs (mg)	0.388	8.05	34.48	65.96	177.16	186.70

Table 4.5: ICP yield results for the GaAs deposit from deposition experiments carried out at a V/III ratio of 50.

The ratio of As:Ga was not stoichiometric, due to the polycrystalline deposit. There was more As than Ga, particularly at 400°C where the ratio was approximately 7:1. At temperatures above this, up to 525° C, the ratio of As:Ga was (1.1–1.3):1. The yield increased with temperature as would be expected in this temperature range where surface reactions limit the growth rate. Figure 4.25 illustrates this more clearly.



Figure 4.25: Total deposit yield (mg) calculated from ICP analysis of the total tube and wafer deposit from experiments carried out with V/III ratio equal to 50 between 400°C and 525°C.

The GaAs yield increased more significantly at the higher temperatures until 500°C. At 525°C, the amount of GaAs was not much more than at 500°C. It was expected that this was due to the fact that the temperature was close to the boundary of the kinetically limited and diffusion limited regimes. This boundary is at 550°C, from which the growth rate is not greatly influenced by an increase in temperature.

Figure 4.26 shows the natural log of GaAs yield against the inverse of temperature (K). From the Arrhenius expression:

$$\frac{\ln(\text{yield}_{\text{GaAs}})}{T^{-1}} = \ln(A) - \frac{E_a}{R}$$
(4.1)

The plot gives $\ln(A)$ at the intercept and $-E_a/R$ is given by the gradient of the line of best fit. However, the plot does not show a strong correlation with Arrhenius parameters, however, a line of best fit has been included on the graph. The fitted line gives a value of -25490 for $-E_a/R$, where $-E_a$ is in J mol⁻¹.



Figure 4.26: Ln deposit yield (mg) against the inverse of temperature (K) calculated from ICP analysis of the total tube and wafer deposit from experiments carried out with V/III ratio equal to 50.

The activation energy calculated from the Arhenius plot does not relate to the activation energy data (Table 2.2, page 55) for the GaAs growth reactions (S33 - S35), and is in general higher in value than the data for all reaction steps.

$$GaCH_3(s_{As}) + As(s_{Ga}) \rightarrow GaAs + CH_3 + s_{Ga} + s_{As}$$
(S33)

$$GaCH_3(s_{As}) + AsH(s_{Ga}) \rightarrow GaAs + CH_4 + s_{Ga} + s_{As}$$
(S34)

$$Ga(s_{As}) + As(s_{Ga}) \rightarrow GaAs + s_{Ga} + s_{As}$$
 (S35)

4.2 GaAs yield results using theoretical model

The calculated mass of GaAs using the model was considered to have realistic value if it was below the mass of TMGa consumed. TMGa was the limiting precursor for GaAs

deposition in the experiments carried out for all temperatures and V/III ratios. From Equation 3.8 (page 69), the overall consumption of TMGa in experimentation was calculated to be 3.40×10^{-4} moles (V/III = 50), 5.67×10^{-4} moles (V/III = 30), and 1.70×10^{-3} moles (V/III = 10). This was the limiting precursor for GaAs, MMGa(s) and Ga(s) production in the deposit.

4.2.1 Model 1

The theoretical model took into account the reaction pathways in Figure 3.17 (page 92) that are represented with black arrows. The reaction rates for the mechanisms with red arrows were small and did not influence the model results. The yield results of GaAs using this model is shown in Table 4.6, representing a V/III ratio of 10.

Temp (°C)	400	425	450	475	500
GaAs (mg)	13.047	0.763	0.338	0.081	0.076

Table 4.6: Species yield in deposit from Model 1 using a V/III ratio of 10.

The results show a reduction in calculated yield with an increase in temperature. This is the opposite effect to what was expected, and cannot be true. The concentrations of the surface intermediates MMGa(s), Ga(s), AsH(s) and As(s) showed the same trend. It was considered possible that the increased rate of reaction with greater temperature for the following reactions was involved:

$^{\cdot}\mathrm{CH}_{3} + \mathrm{H}^{\cdot} + \mathrm{M} \rightarrow \mathrm{CH}_{4} + \mathrm{M}$	(G1)
$\mathrm{H}^{\cdot} + \mathrm{H}^{\cdot} + \mathrm{M} \rightarrow \mathrm{H}_{2} + \mathrm{M}$	(G2)
$^{\cdot}\mathrm{CH}_{3}+^{\cdot}\mathrm{CH}_{3}\rightarrow\mathrm{C}_{2}\mathrm{H}_{6}$	(G3)
$H(s_{Ga}) + H(s_{As}) \rightarrow H_2 + s_{Ga} + s_{As}$	(S15)
$CH_3(s_{As}) + CH_3(s_{Ga}) \rightarrow C_2H_6 + s_{As} + s_{Ga}$	(S16)
$H(s_{Ga}) + CH_3(s_{As}) \rightarrow CH_4 + s_{Ga} + s_{As}$	(S17)

The surface sites were represented by s_{Ga} and s_{As} where they refer to a Ga surface atom and As surface atom respectively. These reactions all involve the radical species in the gas phase and at the surface. The rates for these reactions were high, with the rise in temperature having a significant effect on reactions S15 to S17. The formation of the surface species involved in GaAs growth was dependent upon surface hydrogen and methyl groups. The reaction rates to produce these species were lower with respect to S15 to S17, which was expected to lead to the reduction in GaAs yield when the temperature was increased.

Using the model over the low temperature range to obtain yield results for GaAs that were consistent with that accepted for the kinetically limited regime proved difficult. The reactions between the H^{\cdot} and ^{\cdot}CH₃ radicals in the gas phase and at the surface were known to be important. It was considered that the iteration method in the model had to be modified, but attempts that were made to achieve realistic results was not possible. It was decided to keep the existing model, but exclude reactions G1 to G3, and S15 to S17. With these reactions excluded, yield results for GaAs were large, exceeding the mass consumption for TMGa, which was the precursor with the limiting input concentration. However, the trend for GaAs yield was that expected for the kinetically limited regime, where the deposit mass increased with temperature. It was found that reaction S14 was affecting the results for GaAs production by increasing the yield excessively due to its influence on AsH(s) concentration in the iteration.

$$AsH_3 + s_{Ga} \rightarrow AsH(s_{Ga}) + H_2$$
(S14)

The mathematical representation for the intermediate species had to include reaction pathways involving the formation of a number of different species that were occurring in parallel. Also, the majority of the reactions involved consumption and generation of the radicals H^{\cdot} and ^{\cdot}CH₃. Thus, there was no simple sequencing of the reaction mechanism for GaAs growth, and this made iteration of the expressions for species concentration difficult. Therefore, due to the complexity of the GaAs growth system, one cannot guarantee true representation of the whole process using this existing model. The aim

was to produce a detailed model to replace semi-empirical methods used previously [4.8, 4.9]. This was not achieved using the model in question, but results that were produced from exclusion of G1 to G3 and S15 to S17, with the manipulation of the iteration process involving AsH(s) are presented in Model 2.

The yield results for GaAs with the exclusion of reaction S14 produced very small yields where virtually no deposit would have been present. The first two equations derived for AsH(s) were found to be significantly influenced by the term for S14. This occurred during the iteration process which involved expressions for the intermediate species AsH₂(g), AsH(g), and H(s), as well as AsH(s). When the term for S14 was included only for the first equation derived for AsH(s), realistic GaAs yields were obtained, which were regarded in a second model. Likewise, the iteration of the expression for AsH(s) concentration equation was manipulated by excluding S14 from the second expression in the sequence, which was considered in another valation of the model. The results from these models were very similar for both calculated GaAs yield, and for the concentrations of the intermediate species involved in production of GaAs. These species included surface MMGa, Ga, AsH and As. Thus, only one of these Model variations will be discussed and will be referred to as Model 2.

4.2.2 Model 2

The calculated yield of GaAs increased with temperature and became significant above 475°C, which was in agreement with experimental results (Figure 4.24, page 119). This yield increased substantially as the temperature approached the diffusion-limited regime (550°C to 800°C), which is used for process manufacturing. Table 4.7 shows the calculated GaAs yields at V/III ratios 50, 30 and 10 over the temperature range used in experiments.

Temp (°C)	400	425	450	475	500	525
V/III = 10	0.219	0.263	1.19	5.35	36.82	186.23
V/III = 30	0.100	0.170	0.832	3.60	22.36	93.34
V/III = 50	0.074	0.143	0.710	2.94	16.97	63.34

Table 4.7: Calculated GaAs yield (mg) using Model 2 from 400°C to 500°C.

It can be seen that the model predicts larger yield for lower ratios, where p_{TMGa} was higher (p_{AsH_3} kept constant throughout experiments), in agreement with experimental findings reported earlier in Section **4.1.5**. A clearer representation of the calculated GaAs yield from Model 2 is presented in Figure 4.27.



Figure 4.27: Calculated yield of GaAs at different temperatures and at V/III ratios 10, 30, 50 using theoretical Model 2.

The trend for GaAs production in Model 2 agrees with the model of Tirtowidjojo and Pollard [4.9] who proposed that at temperatures between 500°C and 727°C, the reaction rate between surface MMGa and surface AsH and As-species to form GaAs became the rate-limiting pathway. The exponential increase in calculated GaAs yield and significant increase at 500°C illustrated in Figure 4.27 supports this theory.

Figure 4.28 shows the natural log of calculated GaAs yield (mg) against the inverse of temperature (K). It shows Arrhenius characteristics, and the calculated value of $-E_a/R$ given by the gradient of each fitted line ranges between approximately -37000 and - 45000. The activation energies calculated from the Arrhenius plot are larger than the values obtained from the ICP data, and more so than the values reported in the kinetic data (Table 2.2, page 55). Differences between activation energy values were observed

in the literature [4.8, 4.9], reported for each reaction step. Sometimes these values were an order of magnitude in difference.

However, due to there being no similarities between calculated activation energies from the model and from Table 2.2 (page 55), no conclusion can be made towards what the rate-determining reaction step may be. It is expected that along the temperature range 400°C to 500°C, the rate-determining step is most likely to change at different temperatures. It is assumed that at the higher temperatures towards 500°C the most likely rate-limiting reaction steps involve the surface reactions where GaAs is formed.



Figure 4.28: Log GaAs yield (mg) against the inverse of temperature (K) calculated from Model 2 for V/III ratios 10, 30 and 50.

4.2.2.1 Surface MMGa

The concentration of surface MMGa calculated in Model 2 increased exponentially as it did for the values of GaAs yield. Table 4.8 shows the results.

Temp (°C)	400	425	450	475	500
V/III = 10	7.61x10 ⁻¹⁵	9.03x10 ⁻¹⁵	3.33x10 ⁻¹⁴	1.02x10 ⁻¹³	4.43x10 ⁻¹³
V/III = 30	6.99x10 ⁻¹⁵	1.20x10 ⁻¹⁴	4.91x10 ⁻¹⁴	1.49x10 ⁻¹³	5.87x10 ⁻¹³
V/III = 50	7.17x10 ⁻¹⁵	1.42x10 ⁻¹⁴	5.95x10 ⁻¹⁴	1.76x10 ⁻¹³	6.42x10 ⁻¹³

Table 4.8: Calculated MMGa(s) concentration (mol cm⁻³) using Model 2 from 400°C to 500°C.

Figure 4.29 shows the effect of increasing p_{TMGa} (lower V/III ratio), where MMGa(s) reduced in concentration. It was expected that increasing the partial pressure of TMGa would lead to more MMGa(s) at the surface. The opposite effect was observed, illustrated in Figure 4.29.



Figure 4.29: Calculated concentration of surface MMGa at different temperatures and at V/III ratios 10, 30, 50 using Model 2.

Increasing p_{TMGa} would have the effect of producing more 'CH₃ radicals in the gas phase. This would be expected to increase the production of surface AsH. Greater abundance of both MMGa(s) and AsH(s) would increase the reaction rate between the two species. This has been observed by the increase in calculated GaAs yield with a greater input concentration of TMGa. Consumption of MMGa(s) and AsH(s) would therefore be more prominent, reducing their concentration at the surface. The increased mass of deposited GaAs would catalyze the effect to a greater extent. With a rise in

temperature the surface reactions increase, leading to the greater difference observed at higher temperatures in the model.

Mountziaris and Jensen [4.8] suggested that TMGa and DMGa decomposition became more important from 500°C. The increased calculated MMGa(s) concentration with temperature in this model correlates with their argument. Leys and Veenvliet [4.11] reported that an increase in p_{TMGa} was found to increase the growth rate of GaAs due to increasing the surface coverage of MMGa(s), AsH(s) and As(s). This does not correlate to the MMGa(s) surface coverage in Model 2, but a greater GaAs yield at relative temperatures supports the effect of its increased consumption.

4.2.2.2 Surface Ga

The surface Ga concentration from Model 2 for temperature ranging from 400°C to 500°C and V/III ratio 10 to 50 is shown in Table 4.9.

Temp (°C)	400	425	450	475	500
V/III = 10	5.35x10 ⁻⁸	5.33x10 ⁻⁸	1.44x10 ⁻⁷	2.65x10 ⁻⁷	6.11x10 ⁻⁷
V/III = 30	2.40x10 ⁻⁸	3.35x10 ⁻⁸	9.85x10 ⁻⁸	1.78x10 ⁻⁷	3.68x10 ⁻⁷
V/III = 50	1.73x10 ⁻⁸	2.76x10 ⁻⁸	8.27x10 ⁻⁸	1.46x10 ⁻⁷	2.78x10 ⁻⁷

Table 4.9: Calculated Ga(s) concentration (mol cm⁻³) using Model 2 from 400°C to 500°C.

The increase in surface coverage of Ga became more pronounced with temperature, particularly at the higher V/III ratios. The larger p_{TMGa} produced more Ga(s) in Model 2, which may also explain the related reduction in MMGa(s). More Ga(s) coverage would be a result from a greater rate of MMGa(s) decomposition. The effect would be expected to be more significant at higher temperatures, where its decomposition rate would increase. Figure 4.30 shows these results.



Figure 4.30: Calculated concentration of surface Ga at different temperatures and at V/III ratios 10, 30, 50 using Model 2.

4.2.2.3 Surface AsH

The calculated AsH(s) concentration in the model was high at 400°C, but it decreased from 400°C to 500°C. Table 4.10 and Figure 4.31 show the calculated AsH(s) concentration over the temperature and V/III ratio range used in the experiments.

Temp (°C)	400	425	450	475	500
V/III = 10	3.67x10 ⁻⁷	1.70x10 ⁻⁷	1.00x10 ⁻⁷	7.40x10 ⁻⁸	6.24x10 ⁻⁸
V/III = 30	1.82x10 ⁻⁷	8.22x10 ⁻⁸	4.74x10 ⁻⁸	3.42x10 ⁻⁸	2.86x10 ⁻⁸
V/III = 50	1.31x10 ⁻⁷	5.84x10 ⁻⁸	3.33x10 ⁻⁸	2.38x10 ⁻⁸	1.98x10 ⁻⁸

Table 4.10: Calculated AsH(s) concentration (mol cm⁻³) using Model 3 from 400°C to 500°C.





Figure 4.31: Calculated yield of surface AsH at different temperatures and at V/III ratios 10, 30, 50 using theoretical Model 2.

It was observed by Bergunde and co-workers [4.3], lower wall temperatures in the Aixtron reactor resulted in the parasitic deposit to mainly consist of arsenic. This model is in agreement with the experimental observation and suggests that the reaction pathway towards As-species depositing was more dominant. However, in the Aixtron reactor there was a heated zone much higher than that of the wall temperature. Deposition at the wall could have been straight forward condensation of arsenic, perhaps of the As₂ species [4.12] that desorbs easily from the surface during growth conditions.

The presence of more TMGa in the model resulted in a larger yield of AsH(s). The reason for this was mentioned earlier as either being due to the increased supply of \cdot CH₃ radicals from TMGa decomposition, or it could be due to more Ga-species adsorbed at the surface for the AsH(s) species to bond to. It was expected that a combination of more \cdot CH₃ radicals in the gas phase and more Ga surface sites were the reasons for an increase in AsH(s) in the model. The reduction in AsH(s) at higher temperatures was determined to be due to its increased surface reaction with MMGa(s) or Ga(s) to form GaAs. In addition to this, its decomposition from the surface would become more prominent at higher temperatures.

At low temperatures, the reaction of AsH(s) at the surface to form either GaAs or As(s) was expected to be slow, leading to the large surface coverage of AsH(s) calculated in the model. At higher temperatures, the reactions involving the consumption of AsH(s) and As(s) to produce GaAs would have increased, which was reflected by the exponential increase in GaAs with temperature over the range used in the model.

4.2.2.4 Surface As

The concentration of surface As followed the same trend for AsH(s), as would be expected. This is represented in Table 4.11 and Figure 4.32.

Temp (°C)	400	425	450	475	500
V/III = 10	3.89x10 ⁻¹⁷	9.22x10 ⁻¹⁸	3.13x10 ⁻¹⁸	1.49x10 ⁻¹⁸	8.75x10 ⁻¹⁹
V/III = 30	3.26x10 ⁻¹⁸	7.11x10 ⁻¹⁹	2.24x10 ⁻¹⁹	9.99x10 ⁻²⁰	5.66x10 ⁻²⁰
V/III = 50	9.95x10 ⁻¹⁹	2.10x10 ⁻¹⁹	6.43x10 ⁻²⁰	2.78x10 ⁻²⁰	1.56x10 ⁻²⁰

Table 4.11: Calculated As (s) concentration (mol cm⁻³) using Model 2 from 400°C to 500°C.



Figure 4.32: Calculated concentration of surface As at different temperatures and at V/III ratios 10, 30, 50 using Model 2.

The reduction of As(s) coverage at the surface was to a larger extent when the temperature was increased. The amount of As(s) present in the model was very low in comparison to AsH(s). This would be significant towards its rate of consumption when surface reaction rates increased with temperature. It was also expected that arsenic desorption from the surface was an important factor. Formation of the arsenic dimer (As₂) at the surface and its subsequent desorption would occur more easily at higher temperatures.

At the higher temperatures from 525°C used in the model, the reaction rates were large enough for significant yields of both precursor product-species, resulting in a very large yield of GaAs. The yield of As(s) in the model was always very low and did not change much over the whole temperature range. Parallel reactions with the reaction of As formation at the surface are shown below, where reaction S34 has the larger reaction rate.

$$AsH(s_{Ga}) + AsH(s_{Ga}) \rightarrow 2As + H_2 + 2s_{Ga}$$
(S24)

$$GaCH_3(s_{As}) + AsH(s_{Ga}) \rightarrow GaAs + CH_4 + s_{Ga} + s_{As}$$
(S34)

There are other reactions that involve the consumption of As(s), which may have contributed to its low yield further:

$$GaCH_{3}(s_{As}) + As(s_{Ga}) \rightarrow GaAs + CH_{3} + s_{Ga} + s_{As}$$

$$Ga(s_{As}) + As(s_{Ga}) \rightarrow GaAs + s_{Ga} + s_{As}$$
(S33)
(S35)

The yield results obtained from the model at 300°C was very high for all product species in the deposit. The model does not take into account the formation of the adduct species $H_3As:Ga(CH_3)_3$, which was reported [4.8] to form at room temperature when there was a mixture of TMGa and AsH₃. At temperatures above 400°C it was expected that the concentration of the adduct species was insignificant as the precursors started to decompose at a significant rate. However, at 300°C, there would only be partial decomposition (decomposition of the adduct species was reported [4.8] from 200°C) of

the adduct species. The model therefore did not give useful results at low temperatures where adduct formation was likely as the model did not take the existence of an adduct species into account. The same was the case for higher temperatures, where yields calculated in the model exceeded that possible from the mass consumption of TMGa in experiments. The existing models for GaAs deposition at the higher process temperatures where diffusion of the species was taken into account has been accepted to give successful representation of existing experimental data. The model used in this study only gave realistic yields over the small temperature range between 400 and 500°C.

Reep and Ghandi [4.13] reported that at low temperatures in the kinetically-limited growth regime the species adsorbed at the surface to any significant extent were MMGa(s) and AsH(s). This agrees with Model 2. They proposed that the dissociation of the last \cdot CH₃ from MMGa(s) required a lot of energy and that the rate-limiting step for AsH₃ decomposition was either dissociation of the first H atom or the adsorption of As(s).

The concentrations of the surface species calculated in the model reflected the results from the EDX carried out on the 5 samples, where the concentration of the Ga-species was greater than that of the As-species on the surface. The values or AsH(s) and Ga(s) in the model were similar, but more MMGa(s) was calculated to be present than As(s). The GaAs yield in the model was low in comparison to that calculated from the ICP data. There was a similarity between the result for the amount of GaAs calculated at 525°C, V/III ratio equal to 10 in Model 2, and the ICP data for the same temperature, but V/III ratio equal to 50. The limitation with the model was that only a GaAs yield was obtained and not a ratio between the As and Ga in the deposit.

4.3 Carbon incorporation into GaAs

The model of Mountziaris and Jensen [4.8] included reactions involving gallium carbene $(Ga(CH_3)_xCH_2)$ species that are generally accepted to be involved in the incorporation of

carbon into the GaAs surface during GaAs deposition. The formation of the carbone species involves the reaction of the CH_3 radical reacting with the methyl-Ga species represented in reactions G5 - G7. These can decompose to lose a methyl radical and form a smaller carbone (G11 and G12).

$$Ga(CH_3)_3 + CH_3 \rightarrow Ga(CH_3)_2CH_2 + CH_4$$
(G5)

$$Ga(CH_3)_2 + CH_3 \rightarrow Ga(CH_3)CH_2 + CH_4$$
(G6)

$$Ga(CH_3) + CH_3 \rightarrow GaCH_2 + CH_4 \tag{G7}$$

$$Ga(CH_3)_2CH_2 \rightarrow Ga(CH_3)CH_2 + CH_3$$
(G11)

$$Ga(CH_3)CH_2 \rightarrow GaCH_2 + CH_3 \tag{G12}$$

The carbene species readily react with H \cdot radicals to re-hydrogenate forming methylated-Ga species again (G8 – G10). These reactions were included in the model and were found to make little difference to the concentrations of TMGa and DMGa. Although, the concentration of MMGa was calculated to be very small, and was affected by the concentration of GaCH₂ in the model used in this study. This reaction mechanism (G10) was determined as a minor reaction pathway, although it was still included in the model.

$$Ga(CH_3)_2CH_2 + H^{\cdot} \rightarrow Ga(CH_3)_3$$

$$Ga(CH_3)CH_2 + H^{\cdot} \rightarrow Ga(CH_3)_2$$

$$(G9)$$

$$Ga(CH_3)CH_2 + H^{\cdot} \rightarrow Ga(CH_3)_2$$

$$(G9)$$

$$GaCH_2 + H' \rightarrow GaCH_3$$
 (G10)

There was no data on rate parameters for the incorporation of carbon in the model of Mountziaris and Jensen [4.8]. There was also no proposed mechanism of carbon incorporation. The following surface reactions (S42 - S44) were mentioned in their model, but said not to influence the growth rate of GaAs.

$$GaCH_2 + s_{As} + s_{Ga} \rightarrow GaC + H_2$$
 (S42)

$$Ga(CH_3)CH_2 + s_{As} + s_{Ga} \rightarrow GaC + CH_3 + H_2$$
(S43)

$$Ga(CH_3)_2CH_2 + s_{As} + s_{Ga} \rightarrow GaC + 2(\cdot CH_3) + H_2$$
(S44)
Kuech and Redwing [4.14] proposed a physical mechanism of carbon incorporation (Figure 4.33) based on observations of Jensen and co-workers [4.15] from Fourier transform infrared (FTIR) studies on TMGa decomposition at ultra high vacuum (UHV). They reported the formation of strongly bound CH_2 groups with low surface coverage on a GaAs surface. It was noticed in the observation [4.14] that the concentration of CH_2 reduced in the presence of an arsenic rich surface terminated with hydrogen.



Figure 4.33: Carbon incorporation mechanism proposed by Kuech and Redwing [4.14]

The carbon incorporation was viewed [4.14] as occurring through surface reactions of adsorbed MMGa, leading to GaCH₂ which may react with an exposed surface Ga atom to place a C atom on an As-site. The Ga-CH₂ may be re-hydrogenated to MMGa, or react with an adsorbed AsH to form GaAs and release \cdot CH₃. The model for carbon incorporation was progression from earlier work by Kuech and Veuhoff [4.16], who monitored carbon incorporation into GaAs using photoluminescence. From their experimental results several factors were found to be important for the level of carbon incorporated into the GaAs deposit, these are listed below.

Temperature: Larger growth temperatures resulted in a larger amount of carbon detected at the GaAs surface. The reaction rate for carbon incorporation increased.

1.

- Pressure: When the overall pressure of the system was reduced the level of carbon incorporation decreased. Increased flow velocity reduced the residence time of the GaCH₂ species at the surface.
- V/III ratio: Low AsH₃ to TMGa ratios were observed to always lead to higher carbon incorporation. GaCH₂ species were in greater concentration due to increased TMGa input concentration.
- Orientation: Substrates with more surface As atoms resulted in more carbon being incorporated at the GaAs surface, with substrates with more surface Ga atoms have less carbon incorporated.
- Carrier gas: He was used instead of H₂ using the exact same growth conditions. No difference in the level of carbon incorporated into the GaAs surface when using either carrier gas was observed.

The calculation of the level of carbon incorporated into GaAs during deposition by MOVPE was developed by Kohda and Wada [4.17, 4.18] from a model by Konagai *et al.* [4.19]. They proposed that carbon was incorporated by dissociation of an H atom from MMGa. The model developed by Kohda and Wada [4.17, 4.18] considered the rate equation in which \cdot CH₃ radicals could be incorporated into the GaAs deposit from the reverse reaction of S6 (Equation 4.2), which is represented in Equation 4.5. In Equation 4.4, k_B is the Boltzman constant. The other parameters are discussed in Section 3.4, from Equation 3.28 (page 91).

$$GaCH_3 \xrightarrow{K_t} Ga + CH_3$$
(4.2)

$$[Ga] = k[GaCH_3] \tag{4.3}$$

$$\mathbf{k} = A \exp\left(\frac{-E_a}{\mathbf{k}_{\rm B} \cdot \mathbf{T}}\right) \tag{4.4}$$

$$GaCH_3 \xleftarrow{k_r} Ga + CH_3$$
 (4.5)

$$\frac{d[Ga]}{dt} = k_{f}[GaCH_{3}] - k_{r}[Ga][CH_{3}] = 0$$
(4.6)

The rate equation above is equal to zero in steady growth conditions.

$$[Ga] = \frac{k_f[GaCH_3]}{k_r[\cdot CH_3]}$$
(4.7)

The concentration of carbon may be represented as below.

$$[C] = \frac{[GaCH_3]}{([Ga] + [\cdot CH_3] + [GaCH_3]]} = \left(\frac{K}{[\cdot CH_3]} + \frac{[CH_3]}{[GaCH_3]} + 1\right)^{-1}$$
(4.8)

.

The equilibrium constant, K, represents k_f/k_r (also represented by k_{S6}/k_{S28} in Table 2.2, page 55). The model predicted that carbon incorporation was not only dependent upon growth temperature, but also on CH_3 concentration, as it suppresses Ga-CH₃ dissociation and its increase in concentration was expected [4.18] to increase carbon incorporation.

The calculation of carbon concentration using Equation 4.8 was carried out in Model 2. The equation above does not take into account other surface reactions involving surface Ga, which were included in Model 2. The carbon was assumed to be incorporated from surface MMGa and the non-dissociation of \cdot CH₃. Therefore, the other reactions involving surface Ga were neglected and the expression including the equilibrium constant for k_{S6} and k_{S28} was used to calculate the yield of carbon incorporated into the GaAs deposit. The results are shown in Table 4.12.

V/III ratio	400°C	425°C	450°C	475°C	500°C
10	2.5×10^{-4}	1.1×10^{-4}	4.6x10 ⁻⁵	2.1x10 ⁻⁵	9.6x10 ⁻⁶
30	5.9x10 ⁻⁵	2.4x10 ⁻⁵	1.0x10 ⁻⁵	4.5x10 ⁻⁶	2.0x10 ⁻⁶
50	3.0x10 ⁻⁵	1.2×10^{-5}	4.9x10 ⁻⁶	2.1x10 ⁻⁶	9.6x10 ⁻⁷

Table 4.12: Calculated concentration of carbon (mol. cm⁻³) incorporated into GaAs using Model 2 and Equation 4.7.



Figure 4.34: Graphical representation of the calculated concentration of carbon (mol. cm⁻³) incorporated into GaAs using Model 2 and Equation 4.7.

The results of the model do not give significant concentrations of carbon incorporated into the deposit. However, they do agree with the observations of Kuech and Veuhoff [4.16], where carbon incorporation increased with a decrease in ratio. This is due to there being a larger presence of Ga-species at the surface at small V/III ratios relative to at high V/III ratios. This gives greater probability of the carbon species forming, due to more MMGa being present at the surface. The amount of carbon incorporated also increased with temperature, less difference was calculated for higher temperatures, which was also observed by Kuech and Veuhoff.

4.4 Model using He in replace of H₂ as carrier gas

The theoretical model was tested under the conditions for use of He as carrier gas instead of H_2 . This involved excluding reaction G4.

$$H_2 + \cdot CH_3 \rightarrow CH_4 + H^{\cdot}$$
 (G4)

The result was that the calculated concentration of the \cdot CH₃ radical increased, which in turn raised the surface concentrations for MMGa(s), Ga(s) and As(s), while the AsH(s) concentration and GaAs yield reduced relative to when G4 was included. The calculated concentration of the H^{\cdot} radical did not change much in the model. This was most likely due to the increased reaction of G20 to produce AsH₂, which could then adsorb to the surface forming AsH(s) and releasing H^{\cdot}. The lack of a significant yield of AsH(s) in the model was due to the large presence of \cdot CH₃, which could react with it to form As(s) noted by the large yield of surface As calculated in the model.

 $AsH_3 + CH_3 \rightarrow AsH_2 + CH_4 \tag{G20}$

$$AsH_2 + s_{Ga} \rightarrow AsH(s_{Ga}) + H^{\cdot}$$
(S13)

$$AsH(s_{Ga}) + CH_3 \rightarrow As(s_{Ga}) + CH_4$$
(S23)

It was thought that the calculated concentration of the CH_3 radical was too high in the model. Observations reported [4.16] between experiments carried out using He as carrier gas instead of H₂ suggested that there was no noticeable difference between growth rates or composition of the deposit. These experiments, however, were often carried out at atmospheric pressure where concentrations and residence times of species are greater than at reduced pressure. Collisions between species in the gas phase under these conditions are considerably reduced and growth rate is more dependent upon surface reaction rates. It is expected that the involvement of H₂ would affect the kinetics of the deposition process of GaAs at low temperatures where growth rate is dependent on surface reactions. The high concentration of CH_3 in the model resulted in high concentrations of the carbene species in the gas phase (reactions G5 – G8 and G11, G12). This produced large calculated yields of MMGa(s) and Ga(s) in the model, which exceeded the possible maximum yield for both species. Carbene species are highly reactive and these Ga-carbene species would be no exception, particularly in the gas phase.

The reactions adopted for Ga-carbene formation by Mountziaris and Jensen [4.8] illustrated the presence of carbon incorporation, without suggesting the mechanism or

rate parameters. The mechanism proposed by Kuech and Redwing [4.14] was more suitable, as it involved surface reactions where the carbene species would be more stabilised by adsorbing to the surface. The existence of gas phase Ga-carbene species, suggested by Mountziaris and Jensen [4.8] could be possible, but their reactive nature would lead to rapid reaction with other species. The large concentration of \cdot CH₃ in the model produced a large concentration of Ga-carbene species in the gas phase, which would normally react with H¹ radicals as illustrated in Figure 3.16, page 92. It was determined that when a He carrier gas was used, the reaction of carbene species with other carbene species could be very probable. Figure 4.35 is a proposed reaction mechanism that may occur between carbene species.



Figure 4.35: Proposed reaction between Ga-carbene species.

The reaction in Figure 4.35 would produce a more stable organic-Ga species in the gas phase which would be removed in the exhaust gas. Not all the gas phase Ga-carbene species were expected to react to form methylated-Ga species which could go on to form MMG(s) and Ga(s) species in the deposit, or carbene species at the surface. The large concentration of \cdot CH₃ radicals would promote carbon incorporation as determined by Kohda and Wada [4.18].

Model 2 neglected reactions G1 to G3 and S15 to S17. These involve reactions between the H \cdot and \cdot CH₃ radicals in the gas phase and at the surface. The radicals may adsorb to any surface atom, and as reported by Mountziaris and Jensen [4.8] were likely to be the only species that adsorb to any significant extent. At the surface, most of the reactions involve these species (Figure 3.16, page 92), without the reaction of \cdot CH₃ with H₂, the

reaction of CH_3 at the surface would increase. The carrier gas has the largest concentration in the system, so when He replaces H_2 as the carrier gas, it would be expected that a difference would be observed in the kinetics of the process.

The reactions G1 to G3 and S15 to S17 have large rates and were neglected from the theoretical model due to the effect of the yield results when their rate parameters were included. The kinetic parameters for these reactions were included in the model without the presence of reaction G4. This reduced the surface concentration for MMGa(s), Ga(s) and As(s) significantly, while the yield for GaAs did not change much. The reactions were again neglected, but surface concentrations for MMGa(s), Ga(s) were extremely small.

Carbon incorporation was reported [4.17] to be dependent upon \cdot CH₃ concentration. There were no observed [4.15] differences in carbon incorporation when using either H₂ or He as carrier gas, the concentration of \cdot CH₃ should therefore be similar in He as it is in H₂. Without reaction G4 to produce H \cdot , when using He, the formation of stable compounds like CH₄ and C₂H₆ must increase to compensate for the extra \cdot CH₃ that cannot react with H₂. This reduces the reaction rate of G13, G14 and G19, which were found to have a large impact on AsH₃ decomposition. TMGa and DMGa pyrolitic decomposition was reported to occur more readily than for AsH₃ [4.2, 4.11]. Without reaction G4, compensation for the reduction in rate of reaction G19 would be gained by the increased reaction rate of G20 (AsH₃ + \cdot CH₃).

4.5 Summary

The results for experimentation and theoretical calculations have been demonstrated to show correlation in this investigation and with results reported in the literature. There was an exception produced in the calculations from Model 2, which have been discussed. Chapter 5 concludes this investigation and discusses areas in which the study could be developed further.

4.6 References

- [4.1] J. Nishizawa, T. Kurabayashi, J. Electrochem. Soc. 130, (1983) 413.
- [4.2] S.P. DenBaars, B.Y. Maa, P.D. Dapkus, A.D. Danner, H.C. Lee, J. Crystal Growth 77, (1986) 188.
- [4.3] T. Bergunde, F. Durst, L. Kadinski, Yu.N. Makarov, M. Schafer, M. Weyers; J. Crystal Growth 145 (1994) 630.
- [4.4] R.-Q. Zhang, Y. Lifshitz, S.-T. Lee, Adv. Mater. 7-8 (2003) 15.
- [4.5] M. Imaizumi, M. Adachi, Y. Fujji, Y. Hayashi, T. Soga, T. Jimbo, M. Umeno, J. Crystal Growth, 221 (2000) 688.
- [4.6] T. Bergunde, D. Gutsche, L. Kadinski, Yu. Makarov, M. Weyers; J. Crystal Growth 146, (1995) 564.
- [4.7] K.J. Weeks, S.J.C. Irvine, S. Bland, J. Crystal Growth 257 (2003) 116.
- [4.8] T.J. Mountziaris, K.F. Jensen, J. Electrochem. Soc. 138, (1991) 2426.
- [4.9] M. Tirtowidjojo, R. Pollard, J. Crystal Growth 93, (1988) 108.
- [4.10] T. Bergunde, M. Dauelsberg, L. Kadinski, Yu.N. Makarov, M. Weyers, D. Schmitz, G. Strauch, H. Jurgensen; J. Crystal Growth 170, (1997) 66.
- [4.11] M.R. Leys, H. Veenvliet; J. Crystal Growth 55, (1981) 145.
- [4.12] "Organometallic Vapour-Phase Epitaxy: Practice and Theory", G.B. Stringfellow, Academic Press, 2nd Edition (1999).
- [4.13] D.H. Reep, S.K. Ghandi, J. Electrochem. Soc. 130, (1983) 675.
- [4.14] T.F. Kuech, J.M. Redwing, J. Crystal Growth 145 (1994) 382.
- [4.15] A.V. Annapragada, S. Salim, K.F. Jensen, Mater. Res. Soc. Symp. Proc. 222 (1991) 81.
- [4.16] T.F. Kuech, E. Veuhoff, J. Crystal Growth 68 (1984) 148.
- [4.17] H. Kohda, K. Wada, J. Crystal Growth 135 (1994) 629.
- [4.18] H. Kohda, K. Wada, J. Crystal Growth 167 (1996) 557.
- [4.19] M. Konagai, T. Yamada, T. Akatsuka, K. Sato, E. Tokumitsu, K. Takahashi, J. Crystal Growth 98 (1989) 167.

5.0 Conclusions and further work

5.1 Conclusion

Using laser interferometry to monitor the growth rate of parasitic deposition in a circular tube reactor proved to be difficult due to the curvature of the reflecting surface. The inclusion of a quartz slide was necessary to gain the reflectance data required for monitoring real-time growth rate of the deposition process. Penetration of the deposit on the reactor wall was demonstrated with a 980 nm wavelength laser, following on from the work of Weeks and co-workers [5.1]. A shorter wavelength of 635 nm was found not to penetrate the wall deposit. In cases where the top plate of the reactor is flat, such as the Aixtron reactor, an additional short wavelength laser could be set up whereby penetration to the substrate did not occur enabling only the parasitic deposit to be monitored. The measured growth rates using laser interferometry in this investigation matched growth rates of parasitic deposition calculated by Bergunde and co-workers [5.2]. The maximum growth rate correlated with that measured from experiments carried out at 475°C and 500°C in this study. Calculated growth rates where minimal deposition was observed by Bergunde et al. [5.2] matched measured growth rates reported in this investigation at the lower temperature of 425°C.

Nucleation time was observed to decrease when temperatures were raised. This was due to the larger surface reaction rates. There was less difference in nucleation time between 475°C and 500°C than was observed from 425°C to 450°C. This was in agreement with Denbaars and co-workers [5.3] who determined TMGa decomposition to only be significant above 400°C. The nucleation time did not show correlation with V/III ratio, particularly at low temperature (425°C). The experiment carried out using a p_{TMGa} in the mid V/III ratio range employed had the quickest nucleation time. At higher temperatures there was little difference between all V/III ratios used. This may be due to scratches at the quartz wafer surface, which act as nucleation sites, caused by handling and reuse from experiment to experiment.

The growth rate, observed from the laser reflectance, was greatest when larger temperatures and p_{TMGa} were employed in experiments. The temperature range used was in the kinetic-limited regime, where surface reactions control the growth rate. The reaction rates at the surface increase with temperature. More Ga-species deposited on the quartz surface with larger p_{TMGa} . In addition, more 'CH₃ radicals were released from TMGa decomposition resulting in enhancement of AsH₃ decomposition. Adsorption of As-species increased with a greater amount of surface Ga-species. Increasing the p_{TMGa} was found to increase the growth rate, having more influence at higher temperatures. This correlates with reports from Leys and Veenvliet [5.5] and Mountziaris and Jensen [5.4].

Growth rate data was only obtained when 2-dimensional growth occurred, which did not occur with every experiment. Growth was often 3-dimensional resulting in loss of reflectance intensity. Layered growth depended upon the relative rates of coalescence and vertical island growth. Growth rate data was obtained from laser reflectance measurements from deposition on the quartz slide positioned in the centre of the reactor heated zone when coalescence occurred at a large rate. The absolute reflectance intensity measurements from the reflectance data. This was because laser reflectance is dependent on 2-dimensional growth of the depositing film, where intensity is lost to 3-dimensional growth and curvature of the reflecting surface. The absolute reflectance model may be of more use for epitaxial deposition of thin films, or it may be adapted towards measuring the rate of surface roughening during thin film deposition.

The results that were obtained for measured growth rate were consistent with other reports where growth rate of GaAs increased with an increase in temperature. Deposition only occurred at temperatures above 400°C agreeing with Leys and Veenvliet [5.5] and Nishizawa and Kurabayshi [5.6]. The wall temperature was calculated to be between 300°C and 500°C by Bergunde and co-workers [5.2] in the Aixtron reactor. The arsenic deposition observed at lower temperature, does not correlate with findings from experiments carried out in this study. The deposition of

arsenic on the Aixtron reactor walls was possibly due to simple condensation. The reactor top plate was cooled by a ceiling gas mixture of H_2/Ar increasing the temperature gradient from the heated susceptor to the quartz top plate, where parasitic deposition was observed [5.2]. The quartz walls of the reactor tube used in this study did not have cooled walls as the tube was surrounded by a furnace in the heated zone of the reactor. Condensation of arsenic may have occurred after the furnace, leading towards the exhaust, where the quartz tube was cooled. At this position, cold water was passed through a copper pipe coiled around the quartz tube. The whole wall deposit was analyzed by ICP, thus the deposit species from this section of the tube would have contributed to the total result. There was no way to confirm arsenic condensation at this cooled part of the tube.

XRD analysis of the deposit on the quartz slide showed the deposit to be polycrystalline with either the (111) or (220) orientation for GaAs being preferred. This correlated strongly with XRD data reported by Imaizumi *et al.* [5.7] who deposited GaAs on quartz substrates in the same temperature range from 400°C to 500°C for the purposes of photovoltaic application. Some of the 2 θ position diffraction peaks for GaAs were similar to some orientations in the arsenic rhombohedral, orthorhombic and tetragonal crystal structures. These similarities contributed to only the odd crystal face for arsenic however and it was determined that the crystal structure of the deposit was only attributed to GaAs.

SEM images gave evidence of a 3-dimensional growth mechanism for GaAs deposition on quartz. The formation of a smooth layer depended on the rate of coalescence of the 3-dimensional (island) growth relative to upward growth rate of the forming islands. Where coalescence became more uniform, the laser reflectance oscillated due to the change in deposit thickness. Increased roughening over time reduced the reflectance intensity, as did the increased thickening of the deposit which led to absorption of the laser. There appeared to be a correlation with respect to observed reflectance oscillations and the presence of 2-dimensional growth confirmed by SEM. The relationship between growth rate, temperature and 2-dimensional growth were,

- Larger growth rate with greater p_{TMGa},
- 2-dimensional growth with low V/III ratio and temperature, or when both were high.

It was determined that coalescence occurred when the concentration of Ga-species was high at lower temperatures, and when its concentration was low at higher temperatures. This was also related to arsenic concentration at the surface, which decreased at larger temperatures due to its greater desorption.

Adsorption of Ga-species was observed without the presence of AsH₃ in the system at 450°C and above from a change in the laser reflectance measurements, where a decrease in reflection intensity was a result of Ga-species forming at the quartz surface. At these temperatures, Ga would be a liquid. EDX for five samples, ranging between temperatures 425°C and 500°C including the all three V/III ratios, determined Ga to be in greater concentration at the surface than As. Although the area sampled using this technique was only a small area of the deposit. The larger concentration of Ga was observed in all five samples, including the sample resulting from an experiment carried out at 425°C and V/III ratio of 50. The result from Figure 4.11, page 108 (SEM image) suggested that the Ga-species adsorbed to the surface first, which then enables the Asspecies to adsorb by lowering the energy required for the As-atom to bond to the surface.

The theoretical model produced some interesting results, where GaAs yield increased with temperature and p_{TMGa} as found in the experimental. It also predicted an increase in surface AsH concentration with a decrease in temperature. The calculated concentration of surface MMGa with larger p_{TMGa} decreased, with more difference between V/III ratio at higher temperatures. The model had to be varied when changing the growth conditions from using H₂ to a He carrier gas. Problems arose from the iteration process also, suggesting that further development of the model would be required. The use of

sophisticated software to handle the iteration of the many reaction pathways would increase the accuracy of the model.

Results from the ICP data showed the GaAs yield to have increased with temperature exponentially between 400°C and 500°C, as in the model. The experimental yield was greater than that calculated in the model. The results were close, however, at 525°C where correlation was observed between the model yield and that from experiments. The ratio between gallium and arsenic in the deposit mass measured by ICP was 1:1.3 (Ga:As). This is non-stoichiometric, with a greater presence of arsenic.

5.2 Further work

There were several experiments and analytical techniques that were not carried out which would have complemented the results collected in the investigation. These additional studies may have helped give more insight into the growth mechanism of GaAs at low temperatures. These analytical techniques and further experiments are put forward in this section for continual investigation of this research.

Due to the breakdown of the ICP equipment, data was only obtained from early experiments when a V/III ratio of 50 was employed. Repair of the equipment was not possible and characterization at other institutions was financially, and logistically inconvenient due to the large amount of samples. No data was collected for experiments using V/III ratios 30 and 10, which would have produced a lot of data for comparison to the theoretical model. In addition, deposits from quartz wafers, placed at the centre of the furnace where the laser monitoring was position, and at the exhaust end of the furnace, were also submitted for ICP analysis. There was expected to be a difference in deposit composition between the central wafer and the exhaust wafer. This would be due to gas phase depletion towards the exhaust where less reactive species would deposit on the second quartz wafer.

Repeating the experiments using He instead of H_2 for the carrier gas would produce kinetic data for comparison between the two different processes. Laser interferometry would give immediate information on the growth rate, which would show any differences at any stage within the experiment. *Ex situ* analysis on the deposit would determine any compositional (ICP) and structural differences (SEM, XRD). These experiments could be compared directly to the experiments carried out using H_2 as a carrier gas, where H_2 is known to be involved in the growth process. The noninvolvement of He in the GaAs growth process is expected to be important in the kinetic-limited growth regime.

The flow velocity adopted in the experiments reflected the flow velocity within the Aixtron reactor used by Bergunde and co-workers [5.2] where they observed maximum growth of the parasitic deposit. Other flow velocities were calculated for radial positions in the Aixtron reactor either side of the position where maximum growth was observed. Larger flow velocities increase the dependence of growth rate on surface reactions where residence time is reduced. Where the flow velocity decreased towards the exhaust in the Aixtron reactor, diffusion of the gas phase species became more important. This effect could be investigated and incorporated into the theoretical model for low temperature GaAs deposition.

In this study, p_{AsH_3} was kept constant and the growth rate was investigated as a function of p_{TMGa} as well as temperature. It was reported [4.4] that at V/III ratios < 20, dependence of GaAs growth rate on p_{AsH_3} occurred. The only V/III ratio used in the experimentation below this was 10, where p_{TMGa} was 0.085 mbar. This pressure could be maintained and p_{AsH_3} varied keeping V/III below 20. This would give more insight into the deposition mechanism of AsH₃ and its involvement with H[•] and •CH₃ radicals and other species at low temperatures.

The parasitic deposition is dominated by surface reactions due to the low temperature at which growth occurs. Experiments whereby the quartz surface is treated could be carried out and its effect on deposition observed by *in situ* reflectance monitoring. The

treatment would be analyzed by the nucleation time of the parasitic growth, where large nucleation delay would be tried to be achieved. Once deposition occurred, growth would proceed as in epitaxy.

The iteration process in the model requires development using a software package to cope with the many parallel reaction pathways that occur simultaneously in the growth process. This would produce a single model, which should be able to be used in any experimental condition within the process, such as the exclusion of reaction G4 (\cdot CH₃ with H₂), when a He carrier gas replaces a H₂ one. With further development and refinement of the model, the multi-step reaction process using the steady state approximation could be extended towards the simulation of the growth of other materials. GaN is one such material, another III-V semiconductor that has attracted a lot of interest over recent years.

5.3 References

- [5.1] K.J. Weeks, S.J.C. Irvine, S. Bland, J. Crystal Growth 257 (2003) 116.
- [5.2] T. Bergunde, M. Dauelsberg, L. Kadinski, Yu.N. Makarov, M. Weyers, D. Schmitz, G. Strauch, H. Jurgensen; J. Crystal Growth 170, (1997) 66.
- [5.3] S.P. DenBaars, B.Y. Maa, P.D. Dapkus, A.D. Danner, H.C. Lee, J. Crystal Growth 77, (1986) 188.
- [5.4] T.J. Mountziaris, K.F. Jensen, J. Electrochem. Soc. 138, (1991) 2426.
- [5.5] M.R. Leys, H. Veenvliet; J. Crystal Growth 55, (1981) 145.
- [5.6] J. Nishizawa, T. Kurabayashi, J. Electrochem. Soc. 130, (1983) 413.
- [5.7] M. Imaizumi, M. Adachi, Y. Fujji, Y. Hayashi, T. Soga, T. Jimbo, M. Umeno, J. Crystal Growth, 221 (2000) 688.

Procedure

Experimental start-up:

- Gas supplies to reactor checked, instruments for control turned on and monitoring set.
- Quartz tube put in place and aligned with laser beam, followed by quartz slide alignment.
- N₂ purge flow stopped, system pressure reduced with vacuum pump down to approximately 4.6 mbar (servo valve set to 0 mbar).
- Throttle valve on pump closed, pump turned off to seal vacuum within the reactor tube and gas lines. Pressure monitored to confirm sealed system.
- System brought back up to atmospheric pressure. Servo valve that maintains pressure controlling N₂ over pump set from 0 mbar to 900 mbar. Once 900 mbar reached, servo valve set to close, N₂ input gas still giving a positive flow into system until atmospheric pressure reached, with system opened to vent at atmospheric pressure. Temperature set and left to stabilise.
- Organometallic cooled to 0°C 1 hour before start of experiment.
- Water for cooling coil turned on, system set to 200 mbar using servo valve, with H₂ carrier gas flow.
- Mass flow controllers (MFCs) set for carrier gas and precursor lines.
- Precursors opened to system bypassing the reactor chamber.
- Experiment started when precursors directed to the reactor chamber.

End of experiment:

- Precursors diverted from reactor chamber to chamber bypass.
- Precursors closed to system. Flow left for 10 minutes to remove precursor gases from system.
- Temperature control turned off and furnace left to cool down. Gas switched from H₂ to N₂.
- System brought back up to atmospheric pressure following same method as before.
- N₂ purge set to trickle flow.
- Laser and water cooling turned off.
- When system cooled to room temperature quartz slide and quartz tube removed for analysis, reactor cleaned.

 $MMGa(s) = \frac{k_{S10}[TMGa]\theta_{MMGa(s)} + k_{S9}[DMGa]\theta_{MMGa(s)} + k_{S4}[MMGa(g)]\theta_{MMGa(s)} + k_{S27}[Ga(s)][CH_3(s)] + k_{S28}[Ga(s)][CH_3]]}{k_{S5} + k_{S6} + k_{S33}[As(s)] + k_{S34}[AsH(s)]}$

 $Ga(s) = \frac{k_{S6}[MMGa(s)] + k_{S7}[Ga(g)]\theta_{Ga(g)}}{k_{S8} + k_{S27}[CH_3(s)] + k_{28}[\cdot CH_3] + k_{S35}[As(s)] + k_{S41}[AsH_3(s)]}$

 $AsH(s) = \frac{k_{S11}[AsH(g)]\partial_{AsH(s)} + k_{S13}[AsH_2]\partial_{AsH(s)} + k_{S14}[AsH_3]\partial_{AsH(s)} + k_{S31}[H(s)][As(s)] + k_{S32}[As(s)][H \cdot]}{k_{S12} + k_{S21}[H \cdot] + k_{S20}[H(s)] + k_{S22}[CH_3(s)] + k_{S23}[\cdot CH_3] + 2 \times k_{S24} + k_{S34}[MMGa(s)] + k_{S40}[AsH_3(s)]}$

 $As(s) = \frac{k_{S22}[AsH(s)][CH_3(s)] + k_{S23}[AsH(s)][\cdot CH_3] + k_{S25} \times \frac{1}{2}[As_2]\Theta_{As(s)} + k_{S38}[AsCH_3(s)][H \cdot] + k_{S39}[AsCH_3(s)][H(s)] + k_{S41}[AsH_3(s)][Ga(s)]}{2 \times k_{S26} + k_{S29}[CH_3(s)] + k_{S30}[\cdot CH_3] + k_{S31}[H(s)] + k_{S32}[H \cdot] + k_{S33}[MMGa(s)] + k_{S35}[Ga(s)]}$

Expressions representing surface concentrations of MMGa, Ga, AsH and As.