Analytical models for growth by metal organic vapor phase epitaxy. II. Influence of temperature gradient

Citation for published version (APA):

Sark, van, W. G. J. H. M., Croon, de, M. H. J. M., Janssen, G. J. H. M., & Giling, L. J. (1990). Analytical models for growth by metal organic vapor phase epitaxy. II. Influence of temperature gradient. *Semiconductor Science and Technology*, 5(1), 36-44. <https://doi.org/10.1088/0268-1242/5/1/004>

DOI:

[10.1088/0268-1242/5/1/004](https://doi.org/10.1088/0268-1242/5/1/004)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[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.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Analytical models for growth by metal organic vapour phase epitaxy: II. Influence of temperature gradient

W G J H M van Sark, M H J M de Croon, G Janssen and L J Giling

Department of Experimental Solid State Physics, RIM, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received 31 March 1989, in final form 11 July 1989, accepted for publication 26 July 1989

Abstract. Analytical descriptions are given of the growth rate in metal organic vapour phase epitaxy processes in the medium- and higher-temperature regions, where growth is controlled by diffusional transport through the gas phase and desorption of growth species, respectively. In continuation of part I, where only isothermal problems were considered, the temperature-dependent hydrodynamic behaviour is now investigated. A temperature gradient is introduced and the effect of thermal diffusion on the growth rate is studied, which is significant: a much ($\sim 40\%$) lower depletion is calculated if thermal diffusion is included. Furthermore the influence of surface reactions at high and low temperatures is investigated, resulting in a model in which the cvd number plays an important role. This model allows for the calculation of growth rates in both the diffusion-limited as well as the high-temperature region, where desorption dominates.

1. Introduction

One of the important epitaxy techniques available at present for the growth of III–V compound semiconductors such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ is metal organic vapour phase epitaxy (MOVPE) [1–3]. The theoretical modelling of phenomena occurring in MOVPE reactors, i.e. flow dynamics and depletion effects, is difficult, although several attempts have been made [4–15]. In part I of this series of papers [15] analytical solutions of the partial differential equations that govern the processes involved, were presented for isothermal models and several velocity profiles. It was found that only small errors are introduced if a plug-flow profile is used in the calculation of concentration profile and growth rate. The use of a plug-flow profile facilitates the calculations considerably.

Assumptions also have been made to reduce the three-dimensional partial differential equations to one two-dimensional equation [15]. The flow dynamics are determined by the carrier gas: the amount of growth species on the total gas being small. The velocity and temperature profiles are fully developed and they are considered for mathematical reasons to be established instantaneously at the point where heating is started ($x = 0$). Furthermore the reactor is considered to be of infinite width. An extensive justification of these assumptions was given in [15]. It follows that the concentration

profile is only a function of the axial coordinate x and vertical coordinate y , thus $C(x, y)$. The velocity and temperature profiles are only a function of y , $v(y)$ and $T(y)$, respectively. Isothermal models ($T(y) \equiv T$) were treated already in [15]. In this paper the influence of a temperature gradient in the direction perpendicular to the gas flow is studied. Special attention will be given to thermal diffusion. Furthermore the influence of surface kinetics will be investigated. In this case the CVD number [16, 17] will be introduced. In part III of this series of papers [18] the derived growth model will be confronted with experimental growth results of Si and GaAs; the growth of AlGaAs will be treated in another paper [19].

2. Differential equations and boundary conditions

The partial differential equation that must be solved has already been given in [15]. With the necessary assumptions [15], which are recapitulated above, we have obtained:

$$v(y) \frac{\partial C(x, y)}{\partial x} = \frac{\partial}{\partial y} \left[D(T(y)) \left(\frac{\partial C(x, y)}{\partial y} + (\alpha_T + 1) \frac{C(x, y)}{T(y)} \frac{\partial T(y)}{\partial y} \right) \right] \quad (1)$$

where $C(x, y)$ is the concentration of growth species, $v(y)$ the flow velocity, $D(T(y))$ the binary diffusion coefficient of the group III component, α_T the thermal diffusion factor, $T(y)$ the growth temperature and x, y are the cartesian coordinates.

The boundary conditions are defined as

$$C(0, y) = (T_0/T(y))C_0 \quad 0 \leq y \leq h \quad (2)$$

$$J(x, 0) = kC(x, y)|_{y=0} \quad x > 0 \quad (3)$$

$$J(x, h) = 0 \quad (4)$$

with h the reactor height and where the flux $J(x, y)$ is given by

$$J(x, y) = D(T(y)) \left(\frac{\partial C(x, y)}{\partial y} + (\alpha_T + 1) \frac{C(x, y)}{T(y)} \frac{\partial T(y)}{\partial y} \right) \quad (5)$$

where k denotes the rate constant for a reaction that is limited by surface kinetics, C_0 the input concentration of the group III component and T_0 the temperature at the top of the (water-cooled) reactor [11]. The boundary conditions straightforwardly follow from the assumptions (see [15]). The factor $T_0/T(y)$ in equation (2) is a result of the assumption that the temperature profile is fully developed at $x > 0$. The expansion of the gas must be accounted for in this boundary condition.

In [15] it was found that it is not needed to use a parabolic velocity profile $v(y)$ for the derivation of the concentration profile $C(x, y)$ and the growth rate $R(x)$; in very good approximation it suffices to use a plug-flow velocity profile (velocity independent of the height y in the reactor). In the isothermal case this profile is $v_{iso}(y) = v_0 T/T_0$, where v_0 is the input velocity of the gases at room temperature. In a temperature gradient it is possible to write it in a similar way: $v(y) = v_T$, where the temperature gradient ($\Delta T = T_s - T_0$) is accounted for in the mean velocity v_T , which is calculated in the next section.

It is assumed that the temperature gradient is linear in the y direction [4, 5, 11], so that

$$T(y) = T_s - (T_s - T_0)y/h \quad (6)$$

where T_s denotes the temperature of the substrate and h the height of the reactor.

3. Influence of temperature gradient on flow dynamics and diffusion

3.1. Flow dynamics

In part I [15] it was shown that the calculation of the growth rate with either a plug-flow profile or a parabolic profile yields the same result within 10%. Therefore it was concluded that a plug-flow profile may be used instead of the parabolic profile for the calculation of the growth rate, which simplifies the solution of the various partial differential equations considerably. The presence of a temperature gradient will change the parabolic

profile and therefore it should be carefully checked whether under this condition it is still justified to use a plug-flow profile for the calculation of the growth rate. To this end it is easiest, in a first approximation, to compare the real velocity profile in a temperature gradient with the parabolic profile in the absence of a temperature gradient.

The correct velocity profile in the presence of a temperature gradient can be derived from the continuity and Navier-Stokes equations [20]. First the temperature dependence of the density ρ and the viscosity η of the carrier gas must be determined. The density ρ is inversely proportional with temperature ($\rho \propto 1/T$) so that the average gas velocity v_s (at T) will be higher with respect to the velocity v_0 (at T_0) for $x < 0$. Furthermore the viscosity η is proportional with temperature as $\eta \propto T^{0.7}$ and the gas velocity is inversely proportional with viscosity [20]. The net effect of temperature on the velocity profile can then be determined by solving the following continuity and Navier-Stokes equations:

$$\frac{\partial}{\partial y} \eta_0 \left(\frac{T(y)}{T_0} \right)^{0.7} \frac{\partial v(y)}{\partial y} = \text{constant} \quad (7)$$

$$bhv_0\rho_0 = \int_0^h bv(y)\rho(y) dy = b\rho_0 T_0 \int_0^h (v(y)/T(y)) dy \quad (8)$$

with

$$v(0) = v(h) = 0 \quad (9)$$

and b the reactor width. The calculated velocity profile is shown in figure 1 for $T_s = 1000$ K and $T_0 = 300$ K. Also shown is the parabolic profile for the isothermal case at room temperature [15] and the parabolic profile in a temperature gradient with a constant viscosity. It is clear that the correct velocity profile is a slightly deformed parabola with an increased maximum velocity that is reached at $y/h = 0.57$. This value is also found by Visser

Figure 1. Comparison of velocity profiles. (1) No temperature gradient (constant temperature $T_0 = 300$ K); (2) temperature-dependent density ρ in linear temperature-gradient ($\Delta T = T_s - T_0$, $T_s = 1000$ K), temperature-independent viscosity η ; (3) temperature-dependent density ρ and viscosity η in linear temperature gradient. In cases 1 and 2 (broken curves) the profile is parabolic (equation (7)), while in case 3 (full curve) the profile is a deformed parabola with its maximum at $y/h = 0.57$.

et al [13], who studied the change in flow velocity when a gas is flowing from a cold (entrance) zone to a hot (heated) zone. This was done by solving the three-dimensional Navier-Stokes equations numerically. From figure 1 it is clear that the deviation from the earlier studied parabolic profile is so small that it still is justified—for the same reasons as given in part I [15]—to use a plug-flow profile instead of the (near) parabolic profile for the case of a temperature gradient. However, the mean plug-flow velocity in a temperature gradient must be carefully calculated. This mean flow velocity v_T can be determined from the mass flux through a cross section of the reactor, using the following simplified continuity equation

$$\begin{aligned} \text{flux}|_{x=0} &= \text{flux}|_{x>0} \\ bhv_0\rho_0 &= \int_0^h bv_T\rho(y) dy = bv_T\rho_0 T_0 \int_0^h \frac{1}{T(y)} dy. \end{aligned}$$

This leads to

$$v_T = \frac{(t_s - 1)}{\ln t_s} v_0 \quad (10)$$

where we have defined $t_s = T_s/T_0$. It follows that in practical ($T_s = 1000$ K, $T_0 = 300$ K) situations $v_T \sim 2v_0$.

3.2. Diffusion

The influence of the temperature gradient on the diffusion coefficient $D(T)$ can be determined using the expression [20]

$$D(T(y)) = D_0 \left(\frac{T(y)}{T_0} \right)^\gamma \quad (11)$$

where D_0 is the diffusion coefficient at T_0 and γ the temperature coefficient. The temperature dependence of $D(T)$ is thus determined by the coefficient γ , which ranges for gases between 1.65 and 2.0 [20]. For the growth of (Al)GaAs ex trimethylaluminium (TMA), trimethylgallium (TMG) and arsine (AsH_3) the values of D_0 and γ are experimentally found to be $0.59 \text{ cm}^2 \text{ s}^{-1}$ and 1.7 [21], respectively.

Another temperature-dependent phenomenon is thermal diffusion. This effect is responsible for the concentration differences between hot and cold spots that arise from differences in size and weight of the various molecules. Heavier particles (e.g. TMA, TMG) tend to concentrate in the colder region in the presence of a temperature gradient. This results in a significant lowering of the growth rate [8, 22, 23]. The thermodiffusion process can be described by introducing the thermal diffusion factor α_T [8, 22, 24]. This factor can be calculated in strongly diluted solutions using the rigid-sphere model or Lennard-Jones potentials and the results are generally formulated in graphs [24], where the thermal diffusion factor α_T is depicted as a function of molecular diameters and weights. In the case of the rigid-sphere model the thermal diffusion factor is calculated to be independent of temperature and ranges between 0 and 1.5 in practical situations. As the thermal diffusion factor is only a weak function of temperature and concentration

of the group III component [21, 22] a constant thermal diffusion factor is used in the present calculations.

4. Model 9[†], temperature gradient and thermal diffusion, gas-phase diffusion-limited regime

In order to determine the concentration profile $C(x, y)$ and the growth rate $R(x)$ the partial differential equation (1) needs to be solved. First a coordinate transformation from y to $t = T(y)/T_0$ is performed, using equation (6), which yields (note that the plug-flow profile with $v(y) = v_T$ is used):

$$\begin{aligned} v_T \frac{\partial C(x, t)}{\partial x} &= - \frac{T_s - T_0}{T_0} \frac{1}{h} \frac{\partial}{\partial t} \left[D(t) \left(- \frac{T_s - T_0}{T_0} \frac{1}{h} \right) \right. \\ &\quad \times \left. \left(\frac{\partial C(x, t)}{\partial t} + (\alpha_T + 1) \frac{C(x, t)}{t} \right) \right]. \end{aligned} \quad (12)$$

Substitution of the velocity profile equation (10) and accounting for the temperature dependence of the diffusion coefficient $D(T)$ (equation (11)) then leads to

$$\begin{aligned} \frac{1}{t_s - 1} \frac{1}{\ln t_s} \frac{h^2 v_0}{D_0} \frac{\partial C(x, t)}{\partial x} &= \frac{\partial}{\partial t} \left[t^\gamma \left(\frac{\partial C(x, t)}{\partial t} + (\alpha_T + 1) \frac{C(x, t)}{t} \right) \right]. \end{aligned} \quad (13)$$

Using the separation of variables method ($C(x, t) = X(x)P(t)$) and equating the resulting expression to the constant $-\lambda^2$ gives:

$$C(x, t) = C_0 \sum_{n=1}^{\infty} \alpha_n P(t) X(x) \quad (14)$$

where $X(x)$ is found to be

$$X(x) = \exp \left(- \lambda_n^2 (t_s - 1) \ln t_s \frac{D_0}{v_0 h} \frac{x}{h} \right). \quad (15)$$

$P(t)$ can be found by solving the differential equation

$$\frac{d}{dt} t^\gamma \left(\frac{dP(t)}{dt} + (\alpha_T + 1) \frac{P(t)}{t} \right) = - \lambda^2 P(t). \quad (16)$$

After multiplication with $t^{2-\gamma}$ equation (16) can be rewritten as

$$\begin{aligned} t^2 \frac{d^2 P(t)}{dt^2} + (\gamma + \alpha_T + 1) t \frac{dP(t)}{dt} \\ + [(\gamma - 1)(\alpha_T + 1) + \lambda^2 t^{2-\gamma}] P(t) = 0. \end{aligned} \quad (17)$$

Under certain conditions ($\alpha_T \geq -1$ and $1 \leq \gamma < 2$) the solution is given in terms of Bessel functions of first and second kind and of fractional order [25, 26]

$$\begin{aligned} P(t) &= t^{-(\alpha_T + \gamma)/2} \left[J_{|\alpha_T - \gamma + 2|/(2-\gamma)} \left(\frac{2}{2-\gamma} \lambda_n t^{(2-\gamma)/2} \right) \right. \\ &\quad \left. - \beta_n Y_{|\alpha_T - \gamma + 2|/(2-\gamma)} \left(\frac{2}{2-\gamma} \lambda_n t^{(2-\gamma)/2} \right) \right]. \end{aligned} \quad (18)$$

[†] The model treated here is preceded by 8 models that were described in part I of this series of papers [15], therefore it is referred to as model 9.

The parameters λ_n , α_n and β_n must be determined from the boundary conditions equations (2)–(4), which can be rewritten in this case as

$$P(t_s) = 0 \quad (19)$$

$$\left(\frac{dP(t)}{dt} + (\alpha_T + 1) \frac{P(t)}{t} \right)_{t=1} = 0. \quad (20)$$

Using the following substitutions

$$\begin{aligned} z &= \frac{\lambda_n}{\varepsilon} t^\varepsilon \\ \zeta &= |\alpha_T - \gamma + 2|/(2 - \gamma) \\ \varepsilon &= (2 - \gamma)/2 \\ \theta &= \begin{cases} -(\alpha_T + 1) & \text{if } \alpha_T - \gamma + 2 \geq 0 \\ 1 - \gamma & \text{if } \alpha_T - \gamma + 2 < 0 \end{cases} \end{aligned} \quad (21)$$

it follows

$$P(t) = t^{(\theta + \varepsilon\zeta)} (J_\zeta(z) - \beta_n Y_\zeta(z)) \quad (22)$$

and the derivative of $P(t)$:

$$\begin{aligned} \frac{dP(t)}{dt} &= \theta t^{(\theta + \varepsilon\zeta - 1)} (J_\zeta(z) - \beta_n Y_\zeta(z)) \\ &+ \lambda_n t^{(\theta + \varepsilon\zeta + \varepsilon - 1)} (J_{\zeta-1}(z) - \beta_n Y_{\zeta-1}(z)). \end{aligned} \quad (23)$$

From equations (19) and (22) it follows

$$\beta_n = \frac{J_\zeta[(\lambda_n/\varepsilon)t_s^\varepsilon]}{Y_\zeta[(\lambda_n/\varepsilon)t_s^\varepsilon]}. \quad (24)$$

From equations (20), (22) and (23) it is found that

$$\begin{aligned} (\theta + \alpha_T + 1) \left[J_\zeta\left(\frac{\lambda_n}{\varepsilon}\right) - \beta_n Y_\zeta\left(\frac{\lambda_n}{\varepsilon}\right) \right] \\ + \lambda_n \left[J_{\zeta-1}\left(\frac{\lambda_n}{\varepsilon}\right) - \beta_n Y_{\zeta-1}\left(\frac{\lambda_n}{\varepsilon}\right) \right] = 0. \end{aligned} \quad (25)$$

The parameters λ_n and β_n can be found numerically using equations (24) and (25). Note that in most practical situations ($\alpha_T \geq 0$, $\gamma = 1.7$ [21] and therefore $\theta = -(\alpha_T + 1)$) the first term on the left-hand side in equation (25) equals 0. Boundary condition equation (2) yields

$$C_0 = t^{(2 - \alpha_T - \gamma)/2} C_0 \sum_{n=1}^{\infty} \alpha_n \left[J_\zeta\left(\frac{\lambda_n}{\varepsilon} t^\varepsilon\right) - \beta_n Y_\zeta\left(\frac{\lambda_n}{\varepsilon} t^\varepsilon\right) \right]. \quad (26)$$

The parameter α_n can now be determined using a similar least-squares fit as was described in [15].

The growth rate $R(x)$ is calculated using

$$\begin{aligned} R(x) &\equiv J(x, 0) \\ &= D(T_s) \left(\frac{\partial C(x, y)}{\partial y} + (\alpha_T + 1) \frac{C(x, y)}{T(y)} \frac{\partial T(y)}{\partial y} \right)_{y=0} \end{aligned} \quad (27)$$

and the following equation is finally obtained

$$\frac{R(x)}{v_0 C_0} = \frac{D_0}{v_0 h} \sum_{n=1}^{\infty} A_n \exp\left(-B_n \frac{D_0}{v_0 h} \frac{x}{h}\right) \quad (28)$$

where

$$\begin{aligned} A_n &= \alpha_n \lambda_n \left(\frac{T_s}{T_0} - 1 \right) \left(\frac{T_s}{T_0} \right)^{-\alpha_T/2} \\ &\times \left\{ -J_{\zeta-1} \left[\frac{\lambda_n}{\varepsilon} \left(\frac{T_s}{T_0} \right)^\varepsilon \right] + \beta_n Y_{\zeta-1} \left[\frac{\lambda_n}{\varepsilon} \left(\frac{T_s}{T_0} \right)^\varepsilon \right] \right\} \end{aligned} \quad (29)$$

$$B_n = \left(\frac{T_s}{T_0} - 1 \right) \ln \left(\frac{T_s}{T_0} \right) \lambda_n^2. \quad (30)$$

In comparison with the case where a temperature gradient is absent [15] the influence of the temperature gradient on the growth is represented by three factors: (i) the normalised growth temperature (T_s/T_0); (ii) the temperature dependence of the diffusion coefficient (γ) as found in the parameter ε (equation (21)); (iii) the occurrence of thermal diffusion (α_T).

To quantitate the influence of these parameters they have been varied as follows:

$$1 < T_s/T_0 \leq 5$$

$$1.5 \leq \gamma < 2$$

$$0 \leq \alpha_T \leq 3.5.$$

Results are presented graphically in figures 2–4, where the exponential factor B_1 in the growth rate expression (equation (30)) is plotted as function of T_s/T_0 , γ and α_T . In figure 2 B_1 is shown as a function of the thermal diffusion factor α_T at $T_s/T_0 = 3.0$ for different values of the temperature dependence coefficient γ for diffusion. In figure 3 B_1 is depicted as a function of T_s/T_0 at $\alpha_T = 1.0$ for different values of γ . Figure 4 shows the dependence of B_1 on T_s/T_0 at $\gamma = 1.7$ for different values of α_T .

The use of the first exponential factor B_1 only can be justified on the same grounds as in the isothermal case [15]. A ‘total deposition check’ parameter ω was introduced [15], which is a measure of the amount of growth species that is deposited if a reactor of infinite length is used. If all species are deposited it follows that $\omega = 1$. This parameter ω can be calculated from the expression

Figure 2. Exponential factor $4B_1/\pi^2$ in the growth rate expression equation (28) as a function of the thermal diffusion factor α_T with the temperature coefficient γ for diffusion as a parameter at $T_s/T_0 = 3.0$ showing the strong influence of α_T on the growth rate.

Figure 3. Exponential factor $4B_1/\pi^2$ as a function of T_s/T_0 with γ as parameter at $\alpha_T = 1.0$ showing the modest influence of γ .

Figure 4. Exponential factor $4B_1/\pi^2$ as a function of T_s/T_0 with α_T as parameter at $\gamma = 1.7$ showing the complex influence of T_s/T_0 .

for the growth rate. The number of terms that are used for this calculation is indicated by adding the suffix n to ω . In [15] it was derived that $\omega_n = \sum_{i=1}^n A_i/B_i$. In the absence of a temperature gradient it was found that $\omega_1 = 0.81$, so that it is reasonable to approximate the growth rate using only the first term ($n = 1$). Here, it is found that for all possible combinations of T_s/T_0 , γ and α_T , as given in figures 2–4, the ‘total deposition check’ parameter ω_1 varies between 0.80 and 0.82. Therefore it is again reasonable to approximate the growth rate using only the first term.

The depletion effect is determined by the exponential factors B_n in equation (28), or as we use one term, by B_1 . As can be deduced from the growth-rate expression (equation (28)) a high value of B_n (B_1) results in a strong depletion effect. To determine the influence of a temperature gradient the exponential factor B_1 is divided by the exponential factor that is obtained in the absence of a temperature gradient, i.e. $\pi^2/4$ [15], hence $4B_1/\pi^2$ is plotted in figures 2–4. Thermal diffusion influences the depletion effect strongly, as is clear from figure 2. The depletion effect is weaker for higher values of α_T , which is to be expected: the flux of growth species towards the susceptor decreases as the thermal diffusion effect in-

creases. Therefore the gas phase will be diluted at a lower rate which weakens the depletion effect. At low values of α_T (< 0.5) the depletion effect is stronger if compared with the case where no temperature gradient is present. This is caused by the enhanced diffusion coefficient $D(T)$ as a result of the increased temperature.

The influence of γ on the depletion effect is not so strong, as is shown in figures 2 and 3. The exponential factor increases with increasing γ ; the diffusion of growth species is enhanced for higher values of γ and therefore the depletion effect is stronger.

The influence of T_s/T_0 on the depletion effect is rather complex, as is seen in figures 3 and 4. The depletion effect increases or decreases with an increasing temperature gradient depending on the combination of α_T and γ . Diffusion and thermal diffusion are competing effects: depletion increases as a result of increasing concentrational diffusion due to increasing T_s/T_0 and γ . Depletion decreases as a result of stronger thermal diffusion due to increasing T_s/T_0 and α_T . As long as α_T is small the concentrational diffusion effect is the dominating factor, whereas at high values of α_T the thermal diffusion effect dominates. From the figures it may be deduced that the temperature gradient has little or no effect on the depletion for values of γ and α_T that satisfy the relation $\gamma - \alpha_T \sim 0.8$.

In conclusion, the influence of the temperature gradient on the growth is strong and complex. It influences both the flow dynamics as well as the diffusion of the growth species. It is demonstrated above that especially concentrational diffusion and thermal diffusion are competing effects. Referring to figure 4 one can deduce that in practical situations for the growth of GaAs ($T_s = 1000$ K, $\gamma(\text{TMG}) = 1.7$ [21], $\alpha_T(\text{TMG}) = 1.0$ [8, 23]) the experimentally observed depletion effect will be $\sim 40\%$ weaker if compared with the case where thermal diffusion is neglected. The general effect of thermal diffusion is that it retards the rate of depletion, which results in a better homogeneity of grown layers in the flow direction (x).

5. Model 10, diffusion and surface kinetics

As long as the supply of growth species towards the susceptor is slower than the crystal growth process itself, surface kinetics may be neglected and the growth is diffusion controlled. However, this is not always valid, especially at low- and high-growth temperatures other effects can dominate. For the MOVPE growth of GaAs a lowering of the growth rate is observed at high and low temperatures [1–3, 27, 28]. At high temperatures desorption of growth species may deplete the surface, which results in a lowering of the growth rate [27, 28]. At low temperatures chemical surface reactions or gas-phase reactions are slow. This also causes a lowering of the growth rate [27]. The influence of reactions in the gas phase is treated elsewhere [14, 29]. Thus at high and low temperatures a transition occurs from diffusion-controlled to kinetically controlled growth.

For both the high- and low-temperature region first-

order reaction kinetics can be considered. For the purpose of this paper, we will represent the various surface reactions by only one reaction rate constant k . It will be shown elsewhere [18, 19], that this is possible for the growth of GaAs and AlGaAs. If first-order reaction kinetics are considered, it holds

$$R(x) = kC(x, 0) \quad (31)$$

where k is the reaction rate constant, in which different rate constants of various surface processes, such as adsorption/desorption and reaction of absorbed species, are combined.

The derivation of model 10 is analogous to model 9 though one has to use the more elaborate boundary condition equation (3) instead of equation (19). In a steady-state situation the supply of growth species from the gas phase must equal the amount of species that contributes to the crystal growth process, hence

$$J(x, 0) = kC(x, 0). \quad (32)$$

If the CVD number N_{CVD} [16, 17] is introduced, defined as

$$N_{\text{CVD}} = \frac{hk}{D(T_s)} = \frac{hk}{D_0 t_s^\gamma} \quad (33)$$

and proceeding along the lines as given in the preceding section we finally obtain

$$\left. \frac{\partial C(x, t)}{\partial t} \right|_{t=t_s} + \left(\frac{(\alpha_T + 1)}{t_s} + \frac{N_{\text{CVD}}}{(t_s - 1)} \right) C(x, t_s) = 0. \quad (34)$$

The solution is

$$C(x, t) = C_0 \sum_{n=1}^{\infty} \alpha_n P(t) X(x) \quad (35)$$

with

$$X(x) = \exp\left(-\lambda_n^2 (t_s - 1) \ln t_s \frac{D_0 x}{v_0 h h}\right) \quad (36)$$

$$P(t) = t^{-(\alpha_T + \gamma)/2} \left[J_\zeta\left(\frac{\lambda_n}{\varepsilon} t^\varepsilon\right) - \beta_n Y_\zeta\left(\frac{\lambda_n}{\varepsilon} t^\varepsilon\right) \right] \quad (37)$$

where the substitutions as given in equation (21) are used. Substitution of this solution in equation (34) gives

$$\left(\theta + \alpha_T + 1 + \frac{N_{\text{CVD}}}{(t_s - 1)} t_s \right) \left[J_\zeta\left(\frac{\lambda_n}{\varepsilon} t_s^\varepsilon\right) - \beta_n Y_\zeta\left(\frac{\lambda_n}{\varepsilon} t_s^\varepsilon\right) \right] + \lambda_n t_s^\varepsilon \left[J_{\zeta-1}\left(\frac{\lambda_n}{\varepsilon} t_s^\varepsilon\right) - \beta_n Y_{\zeta-1}\left(\frac{\lambda_n}{\varepsilon} t_s^\varepsilon\right) \right] = 0. \quad (38)$$

Boundary condition equation (4) gives

$$(\theta + \alpha_T + 1) \left[J_\zeta\left(\frac{\lambda_n}{\varepsilon}\right) - \beta_n Y_\zeta\left(\frac{\lambda_n}{\varepsilon}\right) \right] + \lambda_n \left[J_{\zeta-1}\left(\frac{\lambda_n}{\varepsilon}\right) - \beta_n Y_{\zeta-1}\left(\frac{\lambda_n}{\varepsilon}\right) \right] = 0. \quad (39)$$

The parameters λ_n and β_n can be determined from equations (38) and (39). Note again that these equations can be simplified, because in practical situations it holds $\theta = -(\alpha_T + 1)$. The parameter α_n follows from equation

(26), which is repeated here:

$$C_0 = t^{(2-\alpha_T-\gamma)/2} C_0 \sum_{n=1}^{\infty} \alpha_n \left[J_\zeta\left(\frac{\lambda_n}{\varepsilon} t^\varepsilon\right) - \beta_n Y_\zeta\left(\frac{\lambda_n}{\varepsilon} t^\varepsilon\right) \right]. \quad (40)$$

The growth rate $R(x)$ can now be given in exactly the same form as derived earlier (equation 28)):

$$\frac{R(x)}{v_0 C_0} = \frac{D_0}{v_0 h} \sum_{n=1}^{\infty} A_n \exp\left(-B_n \frac{D_0 x}{v_0 h h}\right) \quad (41)$$

but now with other coefficients A_n and B_n :

$$A_n = N_{\text{CVD}} \left(\frac{T_s}{T_0} \right)^{(\gamma-\alpha_T)/2} \alpha_n \left\{ J_\zeta\left[\frac{\lambda_n}{\varepsilon} \left(\frac{T_s}{T_0} \right)^\varepsilon\right] - \beta_n Y_\zeta\left[\frac{\lambda_n}{\varepsilon} \left(\frac{T_s}{T_0} \right)^\varepsilon\right] \right\} \quad (42)$$

$$B_n = \left(\frac{T_s}{T_0} - 1 \right) \ln \left(\frac{T_s}{T_0} \right) \lambda_n^2. \quad (43)$$

The coefficients A_n and B_n both are a function of N_{CVD} , as the λ_n are a function of N_{CVD} through equation (38).

The influence of surface kinetics on the growth is directly determined by the CVD number N_{CVD} . In order to study the effect of this CVD number on the growth rate as well as the effects of the temperature gradient and thermal diffusion, the parameters N_{CVD} , α_T and T_s/T_0 are varied as follows

$$10^{-3} \leq N_{\text{CVD}} \leq 10^3$$

$$0 \leq \alpha_T \leq 3.5$$

$$1 \leq T_s/T_0 \leq 5.$$

The influence of N_{CVD} on the 'total deposition check' parameter ω_n (see §4 and [15]) is presented in figure 5. Both ω_1 (using one term in the calculation) and ω_{10} (ten terms) are shown as a function of N_{CVD} . For large values of N_{CVD} (>100) it is found that $\omega_1 = 0.8$, which is comparable with the results obtained without surface

Figure 5. Deposition check parameters ω_1 and ω_{10} as a function of N_{CVD} . For N_{CVD} values > 1 the growth controlling mechanism changes from surface kinetics (low N_{CVD}) to diffusion controlled (high N_{CVD}). Other parameters are: $\gamma = 1.7$, $\alpha_T = 1.0$, $T_s/T_0 = 3.0$.

kinetics (model 9). The parameter ω_{10} equals 0.98 in this case. The transition from diffusion controlled growth to growth that is controlled by surface kinetics occurs in the region where N_{CVD} is somewhat larger than 1. For small values of N_{CVD} (< 0.1) it is found that $\omega_1 = \omega_{10} = 1.0$, which agrees well with results obtained if one considers only surface kinetics (see models 7 and 8 in [15], where the growth rate can be entirely described by one term). Although it is not shown here, it can be calculated that the results for ω_1 and ω_{10} are nearly independent of the values of the parameters α_T and T_s/T_0 .

The depletion effect is determined by the exponential factors B_n . From the above observations (see also the previous section and [15]) it seems acceptable to use one term in the description of the growth rate. Figure 6 shows the influence of N_{CVD} upon the exponential factor B_1 . It is found that the general behaviour of the exponential factor B_1 as a function of N_{CVD} is independent of the parameters α_T (figure 6) and T_s/T_0 (not shown), however, absolute values for B_1 can differ over a factor of 2. For $N_{\text{CVD}} > 10$ the exponential factor B_1 is independent of N_{CVD} : the growth and depletion is mainly determined by gas-phase diffusion. The horizontal broken lines in figure 6 represent the maximum exponential factor B_1 as calculated with model 9 (no surface kinetics). In the region $10 \geq N_{\text{CVD}} \geq 0.1$ the effect of surface kinetics becomes more and more important. For $N_{\text{CVD}} < 0.1$ the exponential factor B_1 is proportional to N_{CVD} . It can be shown that for $N_{\text{CVD}} \rightarrow 0$ the exponential factor B_1 can be written as

$$B_1 = \frac{\ln t_s^{\alpha_T}}{t_s^{\alpha_T} - 1} t_s^{(\gamma-1)N_{\text{CVD}}}. \quad (44)$$

As was shown above, if surface kinetics controls the growth, one term may be used to describe the growth rate completely. From the definition of $\omega_1 (= A_1/B_1)$ and

Figure 6. The exponential factor B_1 as a function of N_{CVD} with α_T as parameter. For N_{CVD} values > 1 the growth controlling mechanism changes from surface kinetics to diffusion controlled. The horizontal broken lines represent the maximum value of B_1 as calculated with model 9 (no surface kinetics). The sloped broken lines are calculated using an approximated expression for B_1 (equation (44)) that follows from corrected model 7 (surface kinetics only). Other parameters are: $\gamma = 1.7$, $T_s/T_0 = 3.0$.

from the fact that $\omega_1 = 1$ for $N_{\text{CVD}} < 0.1$ it follows that the prefactor A_1 equals B_1 . We therefore find (substituting N_{CVD} by its definition equation (33))

$$\frac{R(x)}{v_0 C_0} = \frac{\ln t_s^{\alpha_T}}{(t_s^{\alpha_T} - 1)t_s} \frac{k(T_s)}{v_0} \exp\left(-\frac{\ln t_s^{\alpha_T}}{(t_s^{\alpha_T} - 1)t_s} \frac{k(T_s)}{v_0} \frac{x}{h}\right). \quad (45)$$

This result equals the one obtained using model 7 (isothermal, surface kinetics only [15]), however, it appears that a correction is needed to include the change in gas-phase concentration at the surface due to the temperature gradient. The sloped broken lines in figure 6 have been calculated with equation (44). It follows that the approximation is already good for $N_{\text{CVD}} < 0.1$.

From figure 6 it can also be concluded that thermal diffusion plays an important role: it weakens the depletion effect considerably, independent of N_{CVD} . The calculations show furthermore that the effects of γ and T_s/T_0 on the depletion are comparable to the effects that occur in the case of model 9 (no surface kinetics).

The effect of surface kinetics is best demonstrated by a plot of growth rate $R(x)h/C_0 D_0$ (dimensionless, cf equation (41)) as a function of $(D_0/v_0 h)(x/h)$ (figure 7): the growth rate decreases with decreasing N_{CVD} . However, the depletion becomes weaker as a result of the fact that the total deposition must remain the same. At very large values of $(D_0/v_0 h)(x/h)$ (> 1) the growth rate at low N_{CVD} values is larger than the growth rate at high N_{CVD} values. The broken lines in figure 7 represent the calculation of the growth rate using ten terms ($n = 10$) in equation (41). It follows that for $(D_0/v_0 h)(x/h) > 0.2$ the curves calculated with one term do not differ from the ones calculated with ten terms, which was already deduced from figure 5. For large N_{CVD} values (> 10) the differences between the two curves may be substantial for the region where $(D_0/v_0 h)(x/h) < 0.2$. This region may be interpreted as a kind of 'entrance region'. In our calculations it was assumed that the entrance region, where the

Figure 7. Growth rate $R(x)h/C_0 D_0$ as a function of $(D_0/v_0 h)(x/h)$ with N_{CVD} as parameter. For N_{CVD} values > 1 the growth controlling mechanism changes from surface kinetics to diffusion controlled. The full lines are calculated using one term in the expression for the growth rate (equation (41)), the broken lines using ten terms. Other parameters are: $\gamma = 1.7$, $\alpha_T = 1.0$, $T_s/T_0 = 3.0$.

velocity and temperature profiles are developed, was of infinitesimal size [15] (note that this does not hold for the concentration profile). In practice, however, this physical entrance region extends several centimetres in the direction of the flow. Therefore calculated growth rates are not expected to be reliable in this region; however, the difference between the growth rate calculated with one term and with ten terms, respectively, is not to be considered important as in practice [11, 15] the condition $(D_0/v_0h)(x/h) > 0.2$ is easily met. Hence calculations with one term are accurate enough.

As a proof of this a practical example is shown in figure 8, where the growth rate $R(x)/v_0C_0$ is depicted as a function of x/h with D_0/v_0h as parameter at $N_{\text{CVD}} = 10$. In our present reactor [11, 15] we calculate $D_0/v_0h \sim 0.05$. We have therefore varied D_0/v_0h over two orders of magnitude to study its influence. In practice D_0/v_0h is varied by changing the gas velocity v_0 appropriately. A high D_0/v_0h (low gas velocity) results in a large depletion effect, whereas a low D_0/v_0h (high gas velocity) results in a weak depletion. The 'entrance region' where it is not allowed to approximate the growth rate by one term, is inversely proportional to D_0/v_0h . This is to be expected as the 'entrance region' ends at $(D_0/v_0h)(x/h) = 0.2$ (see above).

In conclusion, the influence of surface kinetics becomes increasingly important with decreasing N_{CVD} . However, even at low N_{CVD} values, the influence of the gas phase is still present mainly through the temperature gradient as can be seen in equation (45). Layers that are homogeneous in thickness in the axial (x) direction can be obtained if the depletion effect is weak. This can be realised using a sufficiently long reactor so that at large x/h the entrance effects can be neglected. A more elegant solution is the use of a tilted susceptor or a tapered reactor with tilt angle ϕ [11]. The free height above the susceptor then is a function of axial position x as follows: $h(x) = h - x \tan \phi$. It was shown experimentally that a constant growth rate in the axial direction (no depletion) could be obtained on 12 cm of the total length of the susceptor for a tilt angle ϕ of 3.5° [11]. To weaken the

Figure 8. Growth rate $R(x)/v_0C_0$ as a function of x/h with D_0/v_0h as parameter at $N_{\text{CVD}} = 10$ (diffusion controlled). The broken curves are calculated with ten terms. Other parameters are: $\gamma = 1.7$, $\alpha_T = 1.0$, $T_s/T_0 = 3.0$.

depletion effect in reactors with constant height h the parameters D_0/v_0h and N_{CVD} may be further adapted. The parameter D_0/v_0h is in practice changed by changing the velocity v_0 , however, enhancing v_0 is not always advantageous: the depletion effect is weakened, but the entrance region is enlarged. Furthermore the efficiency in the use of metal-organics is decreased and if v_0 is too high, unwanted turbulence effects may occur. Lowering N_{CVD} by adjusting the substrate temperature decreases the depletion effect, but also the growth rate and growth times are therefore enhanced. As surface reactions become more important, the growth rate may become dependent of the crystal orientation. This, however, can be advantageous if one employs anisotropic growth methods to fabricate semiconductor circuits.

6. Conclusion

The influence of a temperature gradient on the growth rate is investigated. Using models based on assumptions made earlier [15] two new models are derived: (i) a model, which describes the growth rate in the diffusion-controlled regime (model 9) and (ii) a model that combines surface kinetics and diffusion of growth species and in which the CVD number plays a key role (model 10). The influence of the temperature gradient on the depletion effect is complex and depends on the combination of the thermal diffusion factor α_T and the temperature coefficient γ of the diffusion coefficient. Diffusion and thermal diffusion are competing effects. This is clearly demonstrated by their combined effect on depletion: depletion decreases as a result of stronger thermal diffusion, whereas depletion increases with γ and the temperature gradient. Furthermore it is found that errors in depletion of $\sim 40\%$ are expected if thermal diffusion is not included in the models. The errors in the growth rate that are a result of depletion changes are of the same order, but vary also with the exact growth conditions, i.e. the position x of the substrates in the reactor.

Surface reactions, both in the low- as well as in the high-temperature region can be included using the CVD number N_{CVD} (model 10). It is found that N_{CVD} has a strong influence on the growth rate and depletion. Lowering N_{CVD} on the one hand weakens the depletion but on the other hand changes the total growth rate considerably. In practice one would prefer to have large growth rates and no (or hardly any) depletion. A compromise can be found if one chooses the right reactor geometry, gas velocity and substrate temperature [1-3, 11, 28, 29]. In order to describe the growth of GaAs and AlGaAs one has to estimate the N_{CVD} from the averaged surface reaction constant k . This will be treated in detail in forthcoming papers [18, 19].

Acknowledgments

This work was performed as a part of the research programme of the Netherlands Technology Foundation

(STW) with financial support from the Netherlands Organisation for Scientific Research (NWO) and by the European Community (EC) under research contract no EN3S-0078-NL.

References

- [1] Ludowise M J 1985 *J. Appl. Phys.* **58** R3
- [2] Kuech T F 1987 *Mater. Sci. Rep.* **2** 1
- [3] Manasevit H M and Simpson W I 1969 *J. Electrochem. Soc.* **116** 1725
- [4] Giling L J 1985 *Crystal Growth of Electronic Materials* ed. E Kaldis (Amsterdam: Elsevier) p 71
- [5] Coltrin M E, Kee R J and Miller J A 1984 *J. Electrochem. Soc.* **131** 425
- [6] Fotiadis D I, Kremer A M, McKenna D R and Jensen K F 1987 *J. Cryst. Growth* **85** 154
- [7] Moffat H and Jensen K F 1986 *J. Cryst. Growth* **77** 108
- [8] Ouazzani J, Chiu K-C and Rosenberger F 1988 *J. Cryst. Growth* **91** 497
- [9] Rhee S, Szekely J and Ilegbusi O J 1987 *J. Electrochem. Soc.* **134** 2552
- [10] Sherman A 1988 *J. Electron. Mater.* **17** 413
- [11] van de Ven J, Rutten G M J, Raaijmakers M J and Giling L J 1986 *J. Cryst. Growth* **76** 352
- [12] Giling L J and van de Ven J 1987 *Advanced Crystal Growth* ed. P M Dryburgh *et al* (New York: Prentice Hall) p 309
- [13] Visser E P, Govers C A M, Giling L J, Kleijn C R and Hoogendoorn C J 1989 *J. Cryst. Growth* **94** 929
- [14] de Croon M H J M and Giling L J 1988 *J. Cryst. Growth* **93** 932
- [15] van Sark W G J H M, Janssen G, de Croon M H J M and Giling L J 1990 *Semicond. Sci. Technol.* **5** 16
- [16] van den Brekel C H J 1977 *Philips Res. Rep.* **32** 118
- [17] van den Brekel C H J and Bloem J 1977 *Philips Res. Rep.* **32** 134
- [18] van Sark W G J H M, de Croon M H J M, Janssen G and Giling L J 1990 *Semicond. Sci. Technol.* **5** at press
- [19] van Sark W G J H M, de Croon M H J M and Giling L J 1989 *J. Appl. Phys.* submitted for publication
- [20] Bird R B, Stewart W E and Lightfoot E N 1960 *Transport Phenomena* (New York: Wiley)
- [21] Suzuki M and Sato M 1985 *J. Electrochem. Soc.* **132** 1684
- [22] Holstein W L 1988 *J. Electrochem. Soc.* **135** 1788
- [23] Jenkinson J P and Pollard R 1984 *J. Electrochem. Soc.* **131** 2911
- [24] Grew K E and Ibbs T L 1952 *Thermal Diffusion in Gases* (London: Cambridge University Press)
- [25] Spiegel M R 1974 *Schaum's Outline of Theory and Problems of Fourier Analysis* (New York: McGraw-Hill)
- [26] *Handbook of Mathematical Functions* 1972 ed. M Abramowitz and I A Stegun (New York: Dover)
- [27] Reep D H and Ghandhi S K 1983 *J. Electrochem. Soc.* **130** 675
- [28] van Sark W G J H M, Janssen G J H M, de Croon M H J M, Giling L J, Arnold Bik W M, Dunselman C P M, Habraken F H P M and van der Weg W F 1988 *J. Appl. Phys.* **64** 195
- [29] de Croon M H J M and Giling L J 1989 *J. Electrochem. Soc.* submitted for publication

List of symbols

A_1, A_i, A_n	pre-exponential factor in growth rate
b	width of reactor
B_1, B_i, B_n	exponential factor in growth rate
$C(x, y), C(x, t)$	concentration of growth species
C_0	input concentration of the group III component
$D(T)$	binary diffusion coefficient of the group III component
D_0	binary diffusion coefficient at $T = T_0$
$h, h(x)$	height of reactor
i	summation parameter
$J(x, y)$	diffusional flux
$J_n(x)$	Bessel function of first kind of order n
$k, k(T)$	reaction rate of surface reaction
n	summation parameter
N_{CVD}	dimensionless CVD number
$P(t)$	y -dependent part of $C(x, y)$
$R(x)$	growth rate
t	normalised temperature ($= T(y)/T_0$)
t_s	normalised growth temperature ($= T_s/T_0$)
T	temperature
ΔT	temperature gradient ($= T_s - T_0$)
$T(y)$	temperature profile
T_0	temperature at top of reactor
T_s	substrate temperature
$v(y)$	velocity profile
v_0	plug-flow velocity
$v_{\text{iso}}(y)$	isothermal velocity profile
v_s	average gas velocity
v_T	corrected plug-flow velocity
x	axial coordinate
$X(x)$	x -dependent part of $C(x, y)$
y	vertical coordinate
$Y_n(x)$	Bessel function of second kind of order n
z	help variable ($= (\lambda_n/\varepsilon)t^\varepsilon$)
α_n	pre-exponential factor
α_T	thermal diffusion factor
β_n	pre-exponential factor
γ	coefficient in temperature dependence of $D(T)$
ε	help parameter ($= (2 - \gamma)/2$)
ζ	help parameter ($= \alpha_T - \gamma + 2 /(2 - \gamma)$)
η	viscosity of gas
η_0	viscosity of gas at $T = T_0$
θ	help parameter $\begin{cases} = -(\alpha_T + 1) & \text{if } \alpha_T - \gamma + 2 \geq 0 \\ = 1 - \gamma & \text{if } \alpha_T - \gamma + 2 < 0 \end{cases}$
λ, λ_n	roots of equation
$\rho, \rho(y)$	density of gas
ρ_0	density of gas at $T = T_0$
φ	tilt angle
ω	total deposition check parameter
$\omega_1, \omega_{10}, \omega_n$	total deposition check parameter using 1, 10, n terms