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Chemical Boundary Layers in CVD

I. Irreversible Reactions

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ABSTRACT

Because of the coupling of the temperature dependence of gas-phase reaction rate constants with the steep temperature gradient, present in most CVD reactors, a thin chemical reaction boundary layer can be defined in the gas phase just above the susceptor. This boundary layer will be present under all operating conditions, including lower pressures and irrespective of the kinetic regime of the deposition reaction or the existence of flow and temperature boundary layers. Using this chemical boundary layer concept it proves to be possible to derive deposition rate equations not only for the gas-phase transport limited regime but also for the gas-phase kinetic regime, or for the case where surface reactions are rate limiting.

Chemical vapor deposition (CVD) is an important technique nowadays to grow electronically active and insulating layers for all kind of solid-state devices. Studies that have been performed over the last few decades have mainly dealt with growth, doping, or technical aspects. Flow dynamics, reactor design, and depletion effects also have received some attention to date, and interest is still growing (1-13), so one can say that understanding in this area is being built up. On the other hand the combination of flow with chemistry is almost a blank area. Because the flow dynamics of the CVD process already is very complex, one is inclined to study these combined phenomena by numerical analysis (1-9). Although the graphical presentation of results obtained by the simulations certainly are instructive, we think that analytical solutions, which describe the chemical/physical behavior, give more direct insight in the physics and chemistry of the CVD process. It is for this reason that we will follow this route in this study. In the recent past, a simplified analytical model, without taking into account temperature gradients, was developed by van de Ven *et al.* (12). This model gives a reasonable description of the depletion behavior in the diffusion-controlled regime of the deposition reaction. An improved version of this theoretical model with a temperature dependent diffusion constant and with thermal diffusion included was published recently (14).

Although the transport problem in the diffusion-limited regime thus seems to be solved in principle, other, and more difficult to solve, problems arise if one considers not only gas-phase transport but also homogeneous reaction kinetics in the CVD system. Steep temperature gradients are present in the reactor and, as most reaction rate constants are strongly temperature dependent, gas-phase reaction rates will be strong functions of the position in the reactor. A complete analytical solution of this problem appears to be next to impossible.

However, in this paper we will present an approximate solution based on a new type of boundary layer model of the system. This boundary layer is caused, not by developing velocity and temperature fields, but by the chemistry itself, coupled to the temperature profile in the reactor. In this respect, the boundary layer model used here, resembles models used to describe combustion processes (15, 16), although one must keep in mind that in the CVD reactor the temperature profile is imposed and in very good approximation not caused by the chemical reactions themselves, in contrast to the above combustion processes.

In this paper we will limit the analysis to reactors where the velocity and temperature fields are fully developed. In a forthcoming paper the model will be applied to cases where physical (flow and temperature) boundary layers do exist as, e.g., in short reactors.

Definition of the Reactor System

Figure 1 gives a schematic overview of the chemical and physical CVD conditions that we will use for our analysis. We take the height of the reactor constant and equal to h

and the width of the reactor much larger than h ; thus, because of the large aspect ratio we may describe this reactor as a two-dimensional system with sufficient accuracy. In this system, the susceptor which is at the bottom wall, is held at temperature T_s , whereas the upper wall is cooled and kept at a constant temperature T_0 , which we suppose to be equal to the inlet temperature of the gases. A large temperature gradient, therefore, exists over the height of the reactor.

The reactant concentrations in the reactor are assumed to be much smaller than the concentration of the carrier gas. From this it follows that the flow and temperature profiles are completely determined by the physical constants of the carrier gas.

The overall flow velocity and the temperature gradient are chosen in such a way that the Reynolds number, Re , satisfies the condition $Re < 2300$. This leads to laminar flow in the reactor (17). Buoyancy forces too are avoided by keeping the cell height so small that the critical Rayleigh (or Grashof) number is not exceeded (17). The flow velocity, however, has not been chosen too small as we want to consider transport in the flow direction to be completely dominated by forced flow, i.e., we neglect diffusion along the axis of the reactor system. End effects in flow and temperature are not taken into account, thus the profiles of the velocity and temperature are completely developed. This will be true after the thermal, and in this case also the velocity, entrance length x_T (11, 18)

$$x_T = 0.40 \cdot Re \cdot Pr \cdot h \quad [1]$$

which for practical reactors is a distance of several to tens of centimeters. Here, Pr is the Prandtl number. For gases it has a value of about 0.7 at all relevant temperatures. The concentration entrance length x_c , defined by the distance necessary to develop the concentration profile by diffusion in a laminar flow, will also be completely developed after the distance x_T . It is shown by van de Ven *et al.* (12) that, for a cell with constant temperature, x_c is smaller than x_T by at least a factor of two.

In order to develop mathematical models for the chemical behavior of the CVD process, we first need to know analytical expressions for the velocity and temperature fields. The temperature profile for a fully developed flow can be calculated by solving the equation for energy conservation

Fig. 1. Schematic model of the reactor conditions used in the calculations.

$$c_p \cdot \rho \cdot v_x \cdot \frac{\partial T}{\partial x} = \frac{\partial}{\partial y} k_0 T^\beta \frac{\partial T}{\partial y} = 0 \quad [2]$$

Here $k_0 T^\beta$ is the temperature-dependent thermal conductivity of the carrier gas, with $\beta \approx 0.7$ (9, 19).

This leads to the temperature profile $T(y)$

$$T(y) = [T_s^{1+\beta} - (T_s^{1+\beta} - T_0^{1+\beta})y/h]^{1/1+\beta} \quad [3]$$

This behavior is depicted in Fig. 2.

The velocity profile $v_x(y)$ for a fully developed flow follows from the continuity equation and from the equation of motion for the carrier gas

$$\frac{d}{dy} \mu_0 T^\gamma \frac{dv_x}{dy} = \text{constant} \quad [4]$$

where $\mu_0 T^\gamma$ is the temperature-dependent dynamic viscosity of the carrier gas, and $\gamma \approx 0.7$ (9, 20). The solution of this equation leads to a distorted parabola with its maximum shifted towards the colder part of the reactor (Fig. 2).

Finally we assume that adsorption of gas-phase species will not occur at the cold upper wall of the reactor but only at the substrate, which is on top of the hot susceptor. This adsorption then will give rise to deposition in the case of doping or growth of the substrate material.

Models and Theoretical Analysis

In this paragraph we present a model which allows us to calculate deposition rates in horizontal CVD reactors for the two cases where the deposition process is limited by highly activated chemical reactions in the gas phase or limited by diffusion through the gas phase coupled with a homogeneous reaction. The main idea behind this model is the notion of a chemical boundary layer, *i.e.*, a layer in the reactor just above the hot susceptor, where chemical reactions mainly take place. This layer is a result of the coupling between the strong temperature dependence of chemical rate constants and the steep, imposed temperature gradient in the reactor. In the following sections it will be shown that, to a first approximation, the layer is independent of reagent concentrations, order of reaction, total pressure, or even of the regime (diffusional or kinetic control) of the growth process.

In the next section and the section on Final solutions of the flux equations we analyze the situation for irreversible reactions for the kinetic-limited regime, treating the thickness of the chemical boundary layer in more detail in the section on The thickness of the chemical boundary layer. In the section on Unidirectional reactions in the gas-phase diffusion-limited regime, we will extend this study to the regime where diffusion through the gas-phase is rate limiting.

Fig. 2. Fully developed flow and temperature profile in a horizontal CVD reactor. $T_s = 1000$ K, $T_0 = 300$ K; v_0 , mean entrance velocity at $T = T_0$.

Unidirectional reactions in the gas-phase reaction-limited regime.—Consider an irreversible reaction which in the general case can be written as

in which R_i are reactants and P_j products. It is assumed that only products P_j adsorb on the substrate leading to growth, *i.e.*, the sticking coefficient of the reactants R_i is taken equal to zero. One now can write continuity equations for reactants and products such as

$$v_x(y) \frac{\partial [R_i]}{\partial x} = \frac{\partial}{\partial y} \mathcal{J}_{D,R_i} - \nu_i k \prod_{l=1}^n [R_l]^{\nu_l} \quad i = 1, n \quad [5]$$

$$v_x(y) \frac{\partial [P_j]}{\partial x} = \frac{\partial}{\partial y} \mathcal{J}_{D,P_j} + \mu_j k \prod_{l=1}^n [R_l]^{\nu_l} \quad j = 1, m \quad [6]$$

where $\mathcal{J}_{D,Q}$ equals the total diffusional flux of component Q (R_i or P_j) in the vertical direction in $\text{mol/m}^2 \text{ s}$ and $[Q]$ the concentration of species Q in mol/m^3 .

An analytical solution of this set of partial differential equations in general appears to be impossible mainly because of the strong temperature, and therefore y , dependence of the reaction rate constant k in the source terms as is sketched in Fig. 3. However, the same steep temperature dependence of the rate constant, *i.e.*, the exponential temperature dependence of the reaction rate makes it possible to apply a reasonable approximation. We proceed as follows. We integrate Eq. [5] and [6] over the cross section of the reactor assuming that the above written reaction will proceed mainly in a boundary layer of thickness δ . The exact form, position, and temperature dependence of the boundary layer at this moment is not relevant at this point. It suffices to assume that a boundary layer exists inside which the reactions occur.

Simple integration gives for the reactant R_i

$$\mathcal{J}_{F,R_i}|_0^h = \mathcal{J}_{D,R_i}|_0^h - \nu_i \int_0^h k \prod_{l=1}^n [R_l]^{\nu_l} dy \quad [7]$$

and for product P_j

$$\mathcal{J}_{F,P_j}|_0^h = \mathcal{J}_{D,P_j}|_0^h + \mu_j \int_0^h k \prod_{l=1}^n [R_l]^{\nu_l} dy \quad [8]$$

Here $\mathcal{J}_{F,Q}|_0^h$ equals the flux of component Q because of the forced flow in the x -direction. The presence of the boundary layer allows us to split up the flux $\mathcal{J}_F$ into two parts and when also for the diffusional fluxes $\mathcal{J}_D$ the integration values are inserted we arrive at

Fig. 3. Normalized reaction rates of a unimolecular reaction with $E_a = 30$ kcal/mol, and 60 kcal/mol, respectively, as function of normalized height in the reactor. $T_s = 1000$ K, $T_0 = 300$ K.

$$\mathcal{J}_{F,R_i}|_0^h + \mathcal{J}_{F,R_i}|_h^h = \mathcal{J}_{D,R_i}(h) - \mathcal{J}_{D,R_i}(0) - \nu_i \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [9]$$

and

$$\mathcal{J}_{F,P_j}|_0^h + \mathcal{J}_{F,P_j}|_h^h = \mathcal{J}_{D,P_j}(h) - \mathcal{J}_{D,P_j}(0) + \mu_j \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [10]$$

Adsorption onto the top of the reactor will not occur. Likewise, the sticking coefficients of R_i are equal to zero. So, Eq. [9] and [10] can be rewritten in a more simplified form, namely

$$\mathcal{J}_{F,R_i}|_0^h + \mathcal{J}_{F,R_i}|_h^h = -\nu_i \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [11]$$

and

$$\mathcal{J}_{F,P_j}|_0^h + \mathcal{J}_{F,P_j}|_h^h = -\mathcal{J}_{D,P_j}(0) + \mu_j \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [12]$$

A closer examination of the flow terms in Eq. [11] and [12] will show that these can be rewritten once again in a more manageable way. The amount of reactant R_i which is lost from the bulk flow i.e., for values of $y \in (\delta, h)$, may easily be shown to be equal to the amount diffusing out of the bulk gas phase into the boundary layer, i.e.

$$\mathcal{J}_{F,R_i}|_h^h = -\mathcal{J}_{D,R_i}(\delta) \quad [13]$$

Similarly, the amount of product P_j which flows out of the reactor for $y \in (\delta, h)$, is equal to the amount of product which diffuses out of the boundary layer into the bulk gas phase. This implies that

$$\mathcal{J}_{F,P_j}|_h^h = -\mathcal{J}_{D,P_j}(\delta) \quad [14]$$

Substituting Eq. [13] and [14] into Eq. [11] and [12] one finally arrives at

$$\mathcal{J}_{F,R_i}|_0^h = \mathcal{J}_{D,R_i}(\delta) - \nu_i \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [15]$$

and at

$$\mathcal{J}_{F,P_j}|_0^h = \mathcal{J}_{D,P_j}(\delta) - \mathcal{J}_{D,P_j}(0) + \mu_j \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [16]$$

The thickness of the chemical boundary layer.—In order to solve this set of equations, one now has to compute the boundary layer thickness δ . It will be shown that this follows from a calculation of the integral in the chemical source term. One therefore needs an expression for the concentrations of R_i as a function of the height in the reactor. These concentrations may be found if one remembers that the overall reaction takes place in the gas-phase reaction limited regime. This means that, after development of temperature and concentration profiles, the diffusion fluxes of R_i will be zero to a very good approximation and also that depletion of the gas phase may be neglected, both because of the slowness of the reaction as compared to diffusion and flow processes. Thus the diffusional flux $\mathcal{J}_{D,R_i}$ in Eq. [5] can be set equal to zero

$$\mathcal{J}_{D,R_i} = D_{R_i} \left\{ \frac{\partial [R_i]}{\partial y} + (\alpha_i + 1) \frac{[R_i]}{T} \frac{\partial T}{\partial y} \right\} = 0 \quad [17]$$

in which α_i equals the thermal diffusion factor of species R_i (note that we have not included the effect of Stefan flow).

It can be shown (Appendix A) that, when care is taken of the mass conservation of the carrier gas and of the R_i species, $[R_i]$ can be written as

$$[R_i(T)] = \frac{\mathcal{R}_i}{\left(\frac{T}{T_0}\right)^{1+\alpha_i}} \quad [18]$$

where

$$\mathcal{R}_i = [R_{i,0}] / \int_0^1 \frac{v_T(y)/v_0}{(T/T_0)^{1+\alpha_i}} d\frac{y}{h} \quad [19]$$

The velocity term in the denominator is of the order 1 and originates from the conservation laws. $[R_{i,0}]$ equals the concentration of R_i at the entrance of the reactor at temperature T_0 and $v_T(y)$ is the velocity profile of the bulk gas phase in the completely developed temperature profile. In Fig. 4 we have plotted $\mathcal{R}_i/[R_{i,0}]$ as a function of T_s/T_0 for two different values of α_i the thermal diffusion factor. The curves are calculated with the assumption of a temperature dependent viscosity in a two-dimensional reactor. In the same figure we also plotted $\mathcal{R}_i/[R_{i,0}]$, using a plug-flow approximation. As can be seen, this much more simple approach will give the right results within about 10% over the complete T_s/T_0 range of interest.

Using the expression for $[R_i(T)]$, we now can evaluate the chemical term at the right-hand side of Eq. [15] and [16] applying the familiar form for the rate constant

$$k = A_0 e^{-E_a/R_g T} \quad [20]$$

and the temperature profile defined earlier

$$T = [T_s^{1+\beta} - (T_s^{1+\beta} - T_0^{1+\beta})y/h]^{1/(1+\beta)} \quad [21]$$

so that

$$\int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy = \int_0^h A_0 e^{-E_a/R_g T} \prod_{i=1}^n \left(\frac{\mathcal{R}_i}{(T/T_0)^{1+\alpha_i}} \right)^{\nu_i} dy \quad [22]$$

It is straightforward, though lengthy, as is given in Appendix B to show that this integral finally leads to an expression of the form

$$\int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy = k_{T_s} \left(\prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \right) \delta \quad [23]$$

where k_{T_s} is the value of the rate constant at the susceptor temperature, and $[R_{i,T_s}]$ in a similar way is the value of $[R_i]$ at T_s .

The constant δ has the dimension of length and can be interpreted as the height of the chemical boundary layer. Its magnitude is given by the exact expression

$$\frac{\delta}{h} = \frac{(1+\beta) \left(\frac{T_s}{T_0}\right)^{1+\beta}}{\left(\frac{T_s}{T_h}\right)^{1+\beta} - 1} \cdot \frac{R_g T_s}{E_a} \times \left\{ \frac{\Gamma\left(\sum_i \nu_i (1+\alpha_i) - \beta - 1, \frac{E_a}{R_g T_s}\right) - \Gamma\left(\sum_i \nu_i (1+\alpha_i) - \beta - 1, \frac{E_a}{R_g T_0}\right)}{\left(\frac{E_a}{R_g T_s}\right)^{\sum_i \nu_i (1+\alpha_i) - \beta - 2} \cdot \exp - E_a/R_g T_s} \right\} \quad [24]$$

where $\Gamma(A, B)$ is an incomplete Γ function (21).

For sufficiently large activation energy, i.e., E_a larger than 100 kJ/mol, Eq. [24] can be approximated within an accuracy of about 5% by Eq. [25]

$$\frac{\delta}{h} = \frac{(1+\beta) \left(\frac{T_s}{T_0}\right)^{1+\beta}}{\left(\frac{T_s}{T_0}\right)^{1+\beta} - 1} \cdot \frac{R_g T_s}{E_a} \approx \frac{16}{E_a (\text{kJ/mol})} \quad [25]$$

taking $\beta = 0.7$ and $T_s = 1000$ K. One should note that this relation shows that the boundary layer thickness in good approximation is independent of the partial orders of reaction ν_i , so that the form of the general reaction [a] is no longer relevant. From Eq. [23] it can be seen that the chemi-

Fig. 4. $R_i/[R_{i,0}]$ as a function of normalized substrate temperature for the thermal diffusion factors $\alpha_i = 1/2$ and $\alpha_i = 1$; (—) exact curve (---) curve calculated with plug-flow approximation.

ical flux is totally confined to a boundary layer. The interpretation is that the chemical reactions indeed can take place inside such a layer. Note, however, that the form of the boundary layer will depend on our interpretation of the right-hand side of Eq. [23]. This will be made clear below.

Final solutions of the flux equations.—For a calculation of the deposition rate we now have to solve the specific partial differential equations given in the beginning of this paper. With our present knowledge we know, that for the case of reaction-limited growth, which we are studying here, we can restrict our analysis to a certain boundary height.

At least two models emerge from the above analysis, both are based on simple interpretations of the end result of the integration in Eq. [23].

The first and simplest model is that the integral $\int_0^h k \Pi[R_i]^n dy$ in Eq. [23] can be replaced by the integral $\int_0^\delta k \Pi[R_i]^n dy$ which leads to the same integration result, when inside the boundary layer the temperature is taken to be constant at a value T_s . This means that the reaction rate $k_{T_s} \Pi[R_{i,T_s}]^n$ is constant inside a boundary layer of thickness δ , outside is zero (see Fig. 5).

In the second model it is assumed that the reaction rate is a linear function in a boundary layer of height 2δ (see Fig. 6). Here the full integral is replaced by the integral $\int_0^{2\delta} k_{T_s}(1 - y/2\delta) \Pi[R_{i,T_s}]^n dy$, which of course also leads to the same end result.

Fig. 5. Normalized reaction rate as function of the normalized height in the reactor with first-order approximation of the chemical boundary layer, i.e., constant reaction rate in boundary layer of width δ : (—) the exact behavior; (---) the first model.

Fig. 6. Normalized reaction rate as function of the normalized height in the reactor with second-order approximation of the chemical boundary layer, i.e., rate varying linearly with height in boundary layer of width 2δ ; (—) the exact behavior; (---) the second model.

Also in this model the reaction occurs in a boundary layer with a height 2δ , but because of the linearly varying rate constant, the reaction rates are more concentrated near the susceptor surface. It will be shown that both models lead to the same deposition rates, although the product concentration profiles will differ in both cases.

Starting now with the first model we see that when we insert Eq. [23] in Eq. [15] and [16] that we have reduced the full temperature-dependent reaction kinetics problem over the total height of the reactor to a temperature independent one in the boundary layer. The reduction of the problem is shown in Fig. 7a and b. In fact, only chemical reactions and diffusional processes in the boundary layer appear to be important. As the chemical reaction bound-

Fig. 7. Schematic overview of full T dependent (a) and of reduced (b) flux problem after introduction of chemical reaction boundary layer. This situation is valid when the growth rate is limited by reactions in the gas phase.

ary layer, in this model, is a region of constant temperature T_s , no thermal diffusion effects have to be taken into account in calculations which deal with diffusion within the boundary layer, in contrast with calculations dealing with diffusion within the bulk of the gas phase. This means that, within this region, neglecting Stefan flow, the diffusional flux is given by

$$\mathcal{J}_{D,Q} = D_Q \frac{\partial[Q]}{\partial y} \quad [26]$$

instead of an equation of the form of Eq. [17].

To obtain the deposition rate in this first-order approximation of the boundary layer one now has to solve the set of partial differential equations, Eq. [27] and [28], inside the boundary layer, i.e., in the region $y \in (0, \delta)$. This set, in fact, is equivalent to the flux equations, Eq. [15] and [16]

$$v_x \frac{\partial[R_i]}{\partial x} = D_{R_i,T_s} \frac{\partial^2[R_i]}{\partial y^2} - \nu_i k_{T_s} \prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \quad [27]$$

$$v_x \frac{\partial[P_j]}{\partial x} = D_{P_j,T_s} \frac{\partial^2[P_j]}{\partial y^2} + \mu_j k_{T_s} \prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \quad [28]$$

Here D_{Q,T_s} equals the diffusion constant of species Q at substrate temperature. Note that the source term has been taken at T_s .

In order to proceed, we now consider the left-hand side of Eq. [27] and [28]. To a very good approximation, one may say that these flow terms in the region $y \in (0, \delta)$ are zero, in the first place because the flow velocity near the walls is almost zero in a laminar flow and, second, because the analysis is for the reaction rate limiting case so that $\partial[R_i]/\partial x$ is small.

Thus for the reaction rate-limited regime we are left with the equation

$$0 = D_{R_i,T_s} \frac{\partial^2[R_i]}{\partial y^2} - \nu_i k_{T_s} \prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \quad y \in (0, \delta) \quad [29]$$

and

$$0 = D_{P_j,T_s} \frac{\partial^2[P_j]}{\partial y^2} + \mu_j k_{T_s} \prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \quad y \in (0, \delta) \quad [30]$$

with the boundary conditions

$$D_{R_i,T_s} \frac{\partial[R_i]}{\partial y} \Big|_0 = 0 \quad D_{P_j,T_s} \frac{\partial[P_j]}{\partial y} \Big|_0 = k_{s,j}[P_j] \Big|_0 \quad [31]$$

$$[R_i]_{y=\delta} = [R_{i,T_s}] \quad D_{P_j,T_s} \frac{\partial[P_j]}{\partial y} \Big|_\delta = 0$$

where $k_{s,j}$ is the first-order rate constant for adsorption and/or surface reaction for species P_j . The last boundary condition is introduced to depict the behavior of the concentration of P_j in the case of a fully developed P_j profile in the bulk of the gas phase. It can be shown that this boundary condition holds after an entrance length x_{P_j} which is of the order of magnitude of x_T , the thermal entrance length as discussed earlier.

The deposition rate is defined by

$$\bar{r} = \sum_{j=1}^m D_{P_j,T_s} \frac{\partial[P_j]}{\partial y} \Big|_0 \quad [32]$$

Because the source terms are small (kinetic-limited regime) in Eq. [29] and [30], implying slow reaction, one finally finds

$$\bar{r} = \sum_{j=1}^m k_{T_s} \cdot \mu_j \prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \cdot \delta \quad [33]$$

Note that Eq. [33] shows that the deposition rate is directly proportional to the thickness of the chemical reaction

boundary layer, and also that the rate equation contains no reference to the adsorption process of the products P_j . Computing product concentrations in the reactor, however, one will find that these are strongly dependent on the adsorption rate constant. This will be pursued in a forthcoming paper.

Having solved the flux equations for the simple model of constant k , we now will proceed by using a linearly variable rate constant k and a constant reagent concentration over the thickness of the chemical boundary layer (model 2). Proceeding along the lines of this section, thereby evaluating the boundary conditions at $y = 0$ and at $y = 2\delta$, one now obtains for the deposition rate

$$\bar{r} = \sum_{j=1}^m k_{T_s} \cdot \mu_j \prod_{i=1}^n [R_{i,T_s}]^{\nu_i} \cdot \delta \quad [34]$$

which is the same rate equation as the one derived for model 1, Eq. [33].

In another paper, where reversible reactions are treated it will be made clear that in that case also the distinction between both models will disappear completely.

Unidirectional reactions in the gas-phase diffusion-limited regime.—To get more insight into the influence of gas-phase reactions in the diffusion-limited deposition regime in CVD, we consider the following reaction occurring in the gas phase

followed by adsorption of the product P . As in the reaction-limited regime one can take the sticking coefficient of R equal to zero as this assumption facilitates the calculations, although it is not necessary to do so. In fact, the above given reaction [b] is a special case of the one studied in sections Unidirectional reactions in the gas-phase reaction-limited regime, The thickness of chemical boundary layer, and Final solutions of the flux equations, but the derivation in principle also is possible for the more elaborated case given there, leading to results similar to those shown below. We can restrict the problem to the simple reaction [b], however, because in all practical cases diffusional limitation of a deposition reaction applies only to one component of the reactant gases.

The main difference, however, with the system studied in the last section is the notion that at high enough temperatures, i.e., in the neighborhood of the susceptor, the reaction becomes very fast as compared to diffusional and flow processes, leading to bulk diffusion as the rate-limiting step in the deposition reaction. The following derivation therefore is given for a reaction which only proceeds at an appreciable rate in a boundary layer of width δ ; this requires a rather large activation energy for the rate constant k . Fast reactions with very low activation energy are simpler to describe without the use of a boundary layer concept and will be treated elsewhere.

Equivalent to Eq. [5] and [6] we have for the continuity equations for reactant R and product P

$$v_x \frac{\partial[R]}{\partial x} = \frac{\partial}{\partial y} \mathcal{J}_{D,R} - k[R] \quad [35]$$

$$v_x \frac{\partial[P]}{\partial x} = \frac{\partial}{\partial y} \mathcal{J}_{D,P} + k[R] \quad [36]$$

From these we find two flux equations, [37] and [38], after integration over a plane perpendicular to the flow direction, when use is made of a boundary layer with thickness δ , and when the same substitutions are made for the fluxes because of flow as given in the section on Unidirectional reactions in the gas-phase reaction-limited regime

$$\mathcal{J}_{F,R}^\delta = \mathcal{J}_{D,R}(\delta) - \int_0^\delta k[R]dy \quad [37]$$

$$\mathcal{J}_{F,R}^\delta = \mathcal{J}_{D,R}(\delta) - \mathcal{J}_{D,P}(0) + \int_0^\delta k[R]dy \quad [38]$$

Similarly as in the case of the reaction-limited regime, the value of the chemical reaction boundary layer thickness δ must follow from the calculation of the integral in the source term of Eq. [37] or [38]. Therefore it is necessary to know the concentration profile of the reactant R for the diffusion-limited case. We cannot proceed in the same manner as given in the section on The thickness of the chemical boundary layer because in the present case $J_{D,R} \neq 0$, however $[R]$ can now be obtained from the simple continuity equation which is valid over almost the full height of the cell. A solution is indeed possible but the analysis is rather complex. We have chosen to proceed first in a more instructive way which leads to the same result. This is done by introducing a mean velocity of the carrier gas, $\bar{v}$, a mean diffusion coefficient of reactant R , $\bar{D}$ and an input concentration $\bar{R}_0$ which is not affected by the temperature gradient in the reactor, thereby neglecting the effects of thermodiffusion. At the end of this section a more rigorous solution will be discussed.

As $k[R]_h \approx 0$ we have for $y \in (\delta, h)$

$$-\bar{v} \frac{\partial [R]}{\partial x} = \bar{D} \frac{\partial^2 [R]}{\partial y^2} \quad [39]$$

with boundary conditions

$$\left. \frac{\partial [R]}{\partial y} \right|_h = 0 \quad [R]_{y=\delta} \approx 0 \quad [40]$$

and $[R]_{x=0} = \bar{R}_0$.

This leads to the desired solution for the concentration of R (12)

$$[R] = \frac{4}{\pi} \bar{R}_0 \sum_{n=0}^{\infty} \frac{\sin \frac{2n+1}{2} \pi y/h}{(2n+1)} \exp - \frac{(2n+1)^2}{4} \pi^2 \frac{\bar{D}x}{\bar{v}h^2} \quad [41]$$

This equation is not really easy to manage but one can write in good approximation for the entrance region $x < x_c$

$$[R] = \bar{R}_0 \operatorname{erf} \left(y/h \cdot \sqrt{\frac{\bar{v}h^2}{4\bar{D}x}} \right) \approx \frac{2}{\sqrt{\pi}} \bar{R}_0 \left\{ \left(\frac{\bar{v}h^2}{4\bar{D}x} \right)^{1/2} y/h - \frac{1}{3} \left(\frac{\bar{v}h^2}{4\bar{D}x} \right)^{3/2} (y/h)^3 \dots \right\} \quad [42]$$

while for $x > x_c$ the familiar expression for the exponential depletion is obtained

$$[R] = \frac{4}{\pi} \bar{R}_0 \sin \left(\frac{\pi}{2} y/h \right) \exp - \frac{\pi^2}{4} \frac{\bar{D}x}{\bar{v}h^2} \quad [43]$$

where x_c is the entrance length of the concentration profile

$$x_c = \frac{h^2 \bar{v}}{16\bar{D}} \quad [44]$$

as given by van de Ven *et al.* (12).

At this point it can be shown that for the diffusion-limited regime, the same chemical boundary height applies as for the kinetic-limited regime. Both approximate equations for the concentration profile (Eq. [42] and [43]) combined with an Arrhenius-type form of the rate constant k and the earlier defined temperatures profile [Eq. [3]] can be inserted into the chemical source integral $\int k R dy$. Integration leads to a form as given in Eq. [45]

$$\int_0^h k[R] dy = k_{T_s} \cdot [R]_h \cdot \delta \quad [45]$$

in which $[R]_h$ is equal to the concentration of R at $y = \delta$ and

$$\delta/h = \frac{(1 + \beta)(T_s/T_0)^{1+\beta} R_g T_s}{(T_s/T_0)^{1+\beta} - 1} \frac{1}{E_a} \quad [46]$$

for sufficiently large activation energy ($E_a > 100$ kJ/mol). This expression is equal to the one obtained [25] in the case of reaction-limited growth.

A more rigorous treatment in the calculation of the reactant concentration R , including a temperature gradient, temperature-dependent diffusion constant, and thermal diffusion, leads to an equation quite similar to Eq. [41]. However, in this case the concentration is a summation not of sine functions, but of Bessel functions of fractional order [14]. It can be shown that the calculation of δ leads to the same approximate result, Eq. [46].

Introduction of Eq. [45] in the flux Eq. [37] and [38] shows that also in the diffusion-limited case one may reduce the T dependent problem to a T independent one at $T = T_s$ with regard to the reaction kinetics of the gas-phase reaction. In principle one now may derive the deposition rate of product P by solving the following set of partial differential equations, Eq. [47]-[50], using the same approximations as used to derive Eq. [29] and [30]

$$-\bar{v} \frac{\partial [R]}{\partial x} = \frac{\partial}{\partial y} \mathcal{J}_{D,R} \quad y \in (\delta, h) \quad [47]$$

$$-\bar{v} \frac{\partial [P]}{\partial x} = \frac{\partial}{\partial y} \mathcal{J}_{D,P} \quad y \in (\delta, h) \quad [48]$$

$$0 = D_{R,T_s} \frac{\partial^2 [R]}{\partial y^2} - k_{T_s} [R] \quad y \in (0, \delta) \quad [49]$$

$$0 = D_{P,T_s} \frac{\partial^2 [P]}{\partial y^2} + k_{T_s} [R] \quad y \in (0, \delta) \quad [50]$$

with boundary conditions

P and R continuous at $y = \delta$ $\mathcal{J}_{D,P} = \mathcal{J}_{D,R} = 0$ at $y = h$

$$\left. \frac{\partial [R]}{\partial y} \right|_{y=0} = 0 \quad D_{P,T_s} \left. \frac{\partial [P]}{\partial y} \right|_{y=0} = k_s [P]_{y=0} \quad [51]$$

The deposition rate is then given by

$$\bar{r} = D_{P,T_s} \left. \frac{\partial [P]}{\partial y} \right|_{y=0} \quad [52]$$

Assuming a large rate constant in a very thin boundary layer, i.e., complete diffusional control because of a highly activated gas-phase reaction, and using mean values for diffusion constants and gas velocity as in Eq. [39], one finds with a high sticking coefficient for P in good approximation

$$\bar{r} = \frac{2\bar{D}}{h} \bar{R}_0 \sum_{n=0}^{\infty} \exp - \frac{(2n+1)^2}{4} \pi^2 \frac{\bar{D}x}{\bar{v}h^2} \quad [53]$$

which is the same rate equation as given by van de Ven *et al.* (12).

Note that this equation shows no reference at all to the reaction product P ; the deposition rate appears to be completely determined by the bulk gas-phase diffusion of reactant R !

Critical Evaluation of Concepts

In this section we will present some arguments about the reality of the proposed boundary layer approach, especially in connection with the assumptions used to derive the definition of the boundary layer width, Eq. [23], and the deposition rate equation, Eq. [33].

From its definition, [23], the boundary layer may be interpreted as a layer of thickness δ where the reaction rate is constant and in which the reaction takes place. This implies that there is no chemical reaction in the bulk of the gas phase. However, as was shown in the section on Final solutions of the flux equations, one can derive the same rate equation for deposition if one takes a linearly varying reaction rate instead of a constant one, in a boundary layer with height 2δ . It was shown that one arrives for both cases

at the same deposition rate equation, Eq. [33]. This is also true when a reaction rate is used which is a power series of the height above the susceptor, provided that the value of the integral in Eq. [23] is not altered and that the rate equals zero from some height ϵ above the susceptor, where ϵ of course should be smaller than or at most equal to the height of the reactor. This implies that the boundary layer width is a rather vague notion: the layer is a fictitious concept and only the integral, Eq. [23], on which the definition of the boundary layer in question rests, is well defined. This exercise proves that within the concept of the chemical boundary layer one can derive deposition rates with good reliability, but also that problems will arise in the calculation of the near exact concentration profiles in the reactor. As the linearly varying reaction rate profile is a better approximation to reality than the block-profile used in the section on Final solutions of the flux equations, it is expected that product concentrations calculated with the former will be more precise than those computed with the latter rate profile. This item will be pursued in a following paper.

Not only the actual thickness of the chemical boundary layers needs a critical evaluation, this also is true for the boundary conditions themselves especially at the top of the boundary layer. This is illustrated as follows.

We have started our considerations by assuming that reactants have a sticking probability equal to zero at the hot substrate surface and that no deposition of gas-phase products occurs at the cold upper wall of the reactor. Dropping the first assumption in the reaction-limited case will hardly give any difficulties in the calculation of the boundary layer width. However, the boundary conditions for the reactants R_i (cf., Eq. [31]) are modified at $x = 0$ and $x = \delta$. This will lead to two terms in the deposition rate equation instead of one. One term corresponds to the deposition of reactant onto the substrate due to adsorption, while the other is related to the original term due to the product formation in the boundary layer. The first term in the practice of MOCVD may be important in the case of AsH_3 or PH_3 adsorption on a Ga-rich (in general III-rich) surface. As long as surplus of arsenic is present in the process, however, this specific adsorption mechanism will not be noticed.

In case we drop the supposition that product P_j will not be adsorbed onto the upper wall of the reactor, we have to take into account that the amount of product P_j that diffuses out of the boundary layer at $y = \delta$, and which is given by $-\mathcal{J}_{D,P_j}(\delta)$ now will be equal to the amount of product P_j which flows out of the reactor for $y \in (\delta, h)$, $\mathcal{J}_{F,P_j}|_{\delta}^h$, plus the amount of product, $-\mathcal{J}_{D,P_j}(h)$, which adsorbs at the upper wall of the reactor. Hence, we arrive at Eq. [54]

$$\mathcal{J}_{F,P_j}|_{\delta}^h - \mathcal{J}_{D,P_j}(h) = -\mathcal{J}_{D,P_j}(\delta) \quad [54]$$

instead of Eq. [14].

Nevertheless, substitution of this equation into Eq. [10] again leads to Eq. [16]

$$\mathcal{J}_{F,P_j}|_{\delta}^h = \mathcal{J}_{D,P_j}(\delta) - \mathcal{J}_{D,P_j}(0) + \mu_j \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy \quad [16]$$

Therefore it follows that the deposition rate still is a function of fluxes in the chemical boundary layer only. This does not mean that the actual growth rate is the same, however. When we solve the flux equations as shown in the section on Final solutions of the flux equations, we then have to use the appropriate boundary condition at the top of the boundary layer for the products P_j instead of the one given in Eq. [31]. In case of completely developed concentration profiles, i.e., approximately after an entrance length x_{P_j} , the boundary condition is now given by

$$D_{P_j,T_s} \frac{\partial [P_j]}{\partial y} \Big|_{\delta} = D_{P_j,T_0} \frac{\partial [P_j]}{\partial y} \Big|_h \quad [55]$$

showing that the amount of product P_j diffusing through the top of the boundary layer is equal to the amount of P_j adsorbing onto the upper wall of the reactor. It is easily

shown that this change in boundary condition will bring about a decrease in rate of deposition onto the substrate by a factor in the order of $(1 - 1/4 \cdot \delta/h)$; so because of the smallness of δ/h , the calculated difference in deposition rates will be quite negligible. Both examples nevertheless prove that the boundary conditions depend on what actually happens in the chemistry of the reactor. The problem is that nobody really knows what is the contribution of each step.

Coupled to the problem depicted here is the description of deposition in reactors with non- or incompletely developed concentration profiles. At $x = 0$, i.e., at the beginning of the susceptor, no products are present in the bulk gas phase. In fully developed flows for large x values a considerable concentration of reaction products has built up in the bulk of the gas phase because of diffusion out the boundary layer. This will contribute to the deposition flux for large values of x . For small reactors this no longer holds. The boundary condition at the top of the reaction boundary layer for these small cells then becomes

$$[P_j]_{T_s}|_{y=\delta} = 0 \quad [56]$$

instead of Eq. [31], leading to a decrease in deposition rate at the substrate surface by a factor of two (in the reaction-limited case) as compared to the one derived in Eq. [33]. The above given boundary condition nevertheless is valid for both diffusion- and kinetic-limited regimes. This problem will be discussed further in a forthcoming paper, describing the low temperature growth of GaAs for reactors with a short susceptor and with a varying height of the temperature boundary layer.

Next the influence of the total pressure on the boundary layer is discussed. In a first approximation, the height of the boundary layer is independent of the total pressure, which follows immediately from Eq. [24]. However, when the carrier gas itself takes part in the chemistry of the process one must be careful, as a change in total pressure also can bring about a change in reaction mechanism itself, especially in the case of complex reaction schemes. Lowering the pressure may also give a change in reaction order and apparent activation energy, e.g., for pseudo-first order reactions at the transition from the high to the low pressure limit. Such changes have to be taken into account when the boundary layer concept is used in calculations of the deposition rates.

The transition from kinetic to diffusion controlled regime by changing the total pressure, has been accounted for in the section on Unidirectional reactions in the gas-phase diffusion-limited regime, where it was proven that the notion of a reaction boundary layer was independent of the reaction regime.

One more interesting result can be obtained from the derivation of the thickness of the chemical reaction boundary layer. As can be seen by comparing Eq. [45] with Eq. [23], the calculation of the reaction boundary layer thickness is in good approximation independent of the kinetic regime of the reaction and also of reactant concentration and reaction order, at least at sufficiently high values of the activation energy. Apparently one may calculate the thickness of the reaction boundary layer from the relation

$$\int_0^h k dy = k_{T_s} \delta \quad [57]$$

an approximation that is good enough for all practical purposes, especially in the light of the uncertainties in the definition of the boundary conditions at the top of the boundary layer where concentration profiles are not well established.

Summary

The semi-analytical description of CVD rates, in which the deposition process is due to activated chemical reactions in the gas phase, leads in a natural way to the concept of a chemical boundary layer. This boundary layer can be regarded as a region in the reactor in which the temperature is so high that the chemical reaction inside this layer proceeds at a much higher rate as compared to the reaction

rate in the bulk of the gas phase. This implies that the chemical reaction boundary layer is closely confined to the hot susceptor surface because of the steep, imposed, temperature gradient in the reactor.

It can be shown that for a good approximation the width of this reaction boundary layer for fully developed flows only is a function of the activation energy of the reaction considered and of parameters defining the temperature gradient in the reactor, viz.

$$\delta = \frac{(1 + \beta) \left(\frac{T_s}{T_0}\right)^{1+\beta}}{\left(\frac{T_s}{T_0}\right)^{1+\beta} - 1} \cdot \frac{R_g T_s}{E_a} \cdot h \quad [58]$$

independent of the order of reaction, of reactant concentrations and of the kinetic regime of the reaction. As the reaction boundary layer is confined to the close neighborhood of the susceptor, the flow velocity in such a layer can be taken to be about zero, whereas from the derivation it also follows that the temperature in the boundary layer is taken equal to the susceptor temperature. Therefore all parameters defining the chemical reaction boundary layer, i.e., gas velocity, temperature, width, are known so that it is possible to use the concept in quantitative calculations of gas-phase reaction rates combined with diffusional fluxes of reactants into and of reaction products out of the reaction boundary layer. From these fluxes one may derive deposition rates after the introduction of sticking coefficients for reactants and products as shown in the preceding section.

In a recently published paper (22) this concept of the chemical boundary layer was used to illustrate the growth and doping of semiconductors.

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APPENDIX A

From Eq. [17]

$$D_{R_i} \left\{ \frac{\partial [R_i]}{\partial y} + (\alpha_i + 1) \frac{[R_i]}{T} \frac{\partial T}{\partial y} \right\} = 0 \quad [17]$$

it follows that

$$\frac{d[R_i]}{[R_i]} = -(\alpha_i + 1) \frac{dT}{T} \quad [A-1]$$

Hence

$$[R_i(T)] = \frac{\mathcal{R}_i}{\left(\frac{T}{T_0}\right)^{1+\alpha_i}} \quad [18]$$

in which $\mathcal{R}_i$ up till now is an unknown but constant concentration.

The total molar flux of compound R_i through a plain perpendicular to the flow direction will be constant because of Eq. [17]. Therefore

$$\int_0^1 v_T(y) \frac{\mathcal{R}_i}{(T/T_0)^{1+\alpha_i}} d\frac{y}{h} = \int_0^1 v_0 [R_{i,0}] d\frac{y}{h} = v_0 [R_{i,0}] \quad [A-2]$$

where v_0 and $[R_{i,0}]$ equal the mean flow velocity and the concentration of R_i , respectively, at the entrance of the reactor at temperature T_0 . $v_T(y)$ is the velocity profile of the bulk gas phase in the developed temperature profile. This latter velocity profile may be calculated from Eq. [4] and the continuity equation of the carrier gas in the developed temperature profile

$$\int_0^1 \frac{v_T(y)/v_0}{T/T_0} d\frac{y}{h} = 1 \quad [A-3]$$

From Eq. [A-2] one finds that

$$\mathcal{R}_i = [R_{i,0}] / \int_0^1 \frac{v_T(y)/v_0}{(T/T_0)^{1+\alpha_i}} d\frac{y}{h} \quad [19]$$

APPENDIX B

In order to derive Eq. [23] and [24] we start with Eq. [22]

$$\int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy = \int_0^h A_0 e^{-E_a/R_g T} \prod_{i=1}^n \left(\frac{\mathcal{R}_i}{(T/T_0)^{1+\alpha_i}} \right)^{\nu_i} dy \quad [22]$$

From the combination of this equation with Eq. [21]

$$T = [T_s^{1+\beta} - (T_s^{1+\beta} - T_0^{1+\beta})y/h]^{1/(1+\beta)} \quad [21]$$

it follows that

$$\begin{aligned} \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy &= A_0 h \prod_i \mathcal{R}_i^{\nu_i} \frac{1 + \beta}{(T_s/T_0)^{1+\beta} - 1} \\ &\times \int_1^{T_s/T_0} \exp \left(-\left(\frac{E_a}{R_g T_0} \cdot \frac{T_0}{T} \right) \right) \frac{1}{\left(\frac{T}{T_0} \right)^{\sum_i \nu_i (1+\alpha_i) - \beta}} dT/T_0 \quad [B-1] \end{aligned}$$

Introducing the help parameter t

$$t = \frac{E_a}{R_g T} \cdot \frac{T_0}{T} \quad [B-2]$$

we can rewrite Eq. [B-1] as

$$\begin{aligned} \int_0^h k \prod_{i=1}^n [R_i]^{\nu_i} dy &= A_0 h \prod_i \mathcal{R}_i^{\nu_i} \frac{1 + \beta}{(T_s/T_0)^{1+\beta} - 1} \\ &\times \frac{1}{\left(\frac{E_a}{R_g T_0} \right)^{\sum_i \nu_i (1+\alpha_i) - \beta - 1}} \cdot \int_{E_a/R_g T_s}^{E_a/R_g T_0} t^{\sum_i \nu_i (1+\alpha_i) - \beta - 2} \exp(-t) dt \quad [B-3] \end{aligned}$$

The right-hand side of this equation is equal to

$$\begin{aligned} A_0 h \prod_i \mathcal{R}_i^{\nu_i} \frac{1 + \beta}{(T_s/T_0)^{1+\beta} - 1} \cdot \frac{1}{\left(\frac{E_a}{R_g T_0} \right)^{\sum_i \nu_i (1+\alpha_i) - \beta - 1}} \\ \times \left\{ \int_{E_a/R_g T_s}^{\infty} t^{\sum_i \nu_i (1+\alpha_i) - \beta - 2} \exp(-t) dt \right. \\ \left. - \int_{E_a/R_g T_0}^{\infty} t^{\sum_i \nu_i (1+\alpha_i) - \beta - 2} \exp(-t) dt \right\} \quad [B-4] \end{aligned}$$

i.e., it equals

$$\begin{aligned} A_0 h \prod_i \mathcal{R}_i^{\nu_i} \frac{1 + \beta}{(T_s/T_0)^{1+\beta} - 1} \cdot \frac{1}{\left(\frac{E_a}{R_g T_0} \right)^{\sum_i \nu_i (1+\alpha_i) - \beta - 1}} \\ \times \left\{ \Gamma \left(\sum_i \nu_i (1 + \alpha_i) - \beta - 1, \frac{E_a}{R_g T_s} \right) \right. \\ \left. - \Gamma \left(\sum_i \nu_i (1 + \alpha_i) - \beta - 1, \frac{E_a}{R_g T_0} \right) \right\} \quad [B-5] \end{aligned}$$

where $\Gamma(A, B)$ is an incomplete Γ function (21).

Hence we find

$$\int_0^h k \prod_{i=1}^n [R_i]^{v_i} dy = \frac{A_0 \exp(-E_a/R_g T_s) \cdot h}{\exp - E_a/R_g T_s} \cdot \times \prod_i \frac{\mathcal{R}_i^{v_i}}{(T_s/T_0)^{v_i(1+\alpha_i)}} \cdot \frac{(T_s/T_0)^{\sum v_i(1+\alpha_i)} \cdot (1+\beta)}{(T_s/T_0)^{1+\beta} - 1} \cdot \times \frac{1}{(E_a/R_g T_s)^{\sum v_i(1+\alpha_i)-\beta-1} \cdot (T_s/T_0)^{\sum v_i(1+\alpha_i)-\beta-1}} \cdot \times \left\{ \Gamma \left(\sum_i v_i(1+\alpha_i) - \beta - 1, \frac{E_a}{R_g T_s} \right) - \Gamma \left(\sum_i v_i(1+\alpha_i) - \beta - 1, \frac{E_a}{R_g T_0} \right) \right\} \quad [\text{B-6}]$$

and thus

$$\int_0^h k \prod_{i=1}^n [R_i]^{v_i} dy = k_{T_s} \prod_i R_{i,T_s}^{v_i} \cdot h \cdot \times \frac{(1+\beta) \left(\frac{T_s}{T_0} \right)^{1+\beta}}{\left(\frac{T_s}{T_0} \right)^{1+\beta} - 1} \cdot \frac{R_g T_s}{E_a} \cdot \times \left\{ \frac{\Gamma \left(\sum_i v_i(1+\alpha_i) - \beta - 1, \frac{E_a}{R_g T_s} \right) - \Gamma \left(\sum_i v_i(1+\alpha_i) - \beta - 1, \frac{E_a}{R_g T_0} \right)}{\left(\frac{E_a}{R_g T_s} \right)^{\sum v_i(1+\alpha_i)-\beta-2} \cdot \exp - E_a/R_g T_s} \right\} \quad [\text{B-7}]$$

This last equation can be written as Eq. [23]

$$\int_0^h k \prod_{i=1}^n [R_i]^{v_i} dy = k_{T_s} \left(\prod_{i=1}^n [R_{i,T_s}]^{v_i} \right) \delta \quad [23]$$

with δ as defined in Eq. [24].

LIST OF SYMBOLS

A_0	pre-exponential factor of rate constant k in units of mol/m ³ and seconds
c_p	heat capacity of the carrier gas at constant pressure, J/kg K
$\bar{D}$	mean diffusion coefficient of reactant R , m ² /s
D_Q	diffusion constant of species Q , m ² /s
D_{Q,T_s}	value of D_Q at temperature T_s , m ² /s
E_a	Arrhenius activation energy rate of constant k , J/mol
h	height of reactor, m
$\mathcal{J}_{D,Q}, \mathcal{J}_{D,Q}(y)$	total diffusional flux of component Q perpendicular to the susceptor, mol/m ² s
$\mathcal{J}_{F,Q}$	flux of component Q because of forced flow parallel to the susceptor, mol/m ² s
k	gas-phase reaction rate constant in units of mol/m ³ and s
$k_0 T^{\beta}$	thermal conductivity of the carrier gas at temperature T , J/m s K
$k_{s,j}$	first-order rate constant for adsorption and/or surface reaction of species P_j , m/s
k_{T_s}	value of k at temperature T_s in units of mol/m ³ and s
P, P_j	product(s)
$[P], [P_j]$	concentration of product, mol/m ³
R, R_i	reactant(s)
$[R], [R_i]$	concentration of reactant (mol/m ³)
R_g	gas constant, J/mol K
$[R_{i,T_s}]$	concentration of reactant R_i at temperature T_s , mol/m ³
$\mathcal{R}_i$	concentration of reactant R_i at the upper wall of the reactor in a completely developed reactant concentration profile in case of negligible gas phase and surface reaction rates, mol/m ³

$\bar{R}_0$	mean input concentration of the reactant R at temperature T_0 , mol/m ³
r	deposition rate, mol/m ² s
$T, T(y)$	temperature profile in the reactor perpendicular to the susceptor, K
T_0	temperature at the entrance and at the upper wall of the reactor, K
T_s	temperature of susceptor, K
v	mean flow velocity of the carrier gas in the reactor parallel to the susceptor, m/s
v_0	mean flow velocity of the carrier gas at the entrance of the reactor at temperature T_0 , m/s
$v_x, v_x(y)$	velocity profile of the carrier gas parallel to the susceptor, m/s
t	help parameter
x	Cartesian coordinate parallel to the susceptor, m
x_c	concentration entrance length of reactor, m
x_T	thermal entrance length of reactor, m
y	Cartesian coordinate perpendicular to the susceptor, m
α_i	thermal diffusion factor of reactant R_i
β	coefficient of temperature dependence of the thermal conductivity of the carrier gas
γ	coefficient of temperature dependence of the dynamic viscosity of the carrier gas
δ	height of the chemical boundary layer, m
$\mu_0 T^{\gamma}$	dynamic viscosity of the carrier gas, kg/m s
μ_j	stoichiometric coefficient of product P_j
ν_i	stoichiometric coefficient of reactant R_i
ρ	density of the carrier gas, kg/m ³

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Conduction Mechanism of Leakage Current in Ta₂O₅ Films on Si Prepared by LPCVD

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ABSTRACT

Electrical properties and conduction mechanisms of leakage current of tantalum pentoxide (Ta₂O₅) films have been studied. Ta₂O₅ films were deposited by cold wall-type, low-pressure chemical vapor deposition (LPCVD), and then annealed at temperatures ranging from 600° to 900°C in O₂. The leakage current flowing through Ta₂O₅ films decreases drastically following the annealing. The conduction mechanism in the films annealed below 800°C is dominated by hopping conduction at room temperature. On the other hand, Fowler-Nordheim tunneling conduction becomes predominant for films annealed above 850°C. The decrease in leakage current with increasing annealing temperature can be mainly explained by a reduction in the carrier density, originating from defects in the films, such as dangling bonds.

There is great interest in Ta₂O₅ films because of their potential applications as dielectric films to storage capacitors in memory cells and gate insulators in ultra-large-scale integrated circuits (ULSIs). Ta₂O₅ films have a large relative dielectric constant of 20-25 compared with SiO₂. However, large leakage currents in Ta₂O₅ films limit applications to ULSIs in terms of storage characteristics.

Several studies have been reported on electrical properties of Ta₂O₅ films. Although as-deposited sputtered Ta₂O₅ films have low leakage current in an amorphous state, the leakage current is drastically increased by high-temperature annealing (1-3). Because of this fact, the usage of sputtered Ta₂O₅ films is not compatible with conventional ULSI processes at the present stage. Understanding of the conduction mechanism of the leakage current is very important to improving the properties of films. Oehrlein *et al.* reported on the conduction mechanism for thermally oxidized Ta films deposited by vacuum evaporation (2, 3), and Banerjee *et al.* also reported on sputtered Ta₂O₅ films with an interfacial SiO₂ layer (4).

We have reported previously on the preparation method and electrical characteristics of Ta₂O₅ films deposited by cold wall-type, low-pressure chemical vapor deposition (LPCVD) (5). In the previous paper, we have demonstrated how to obtain Ta₂O₅ films with high relative dielectric constants of 25-35 and low leakage currents by high-temperature annealing in O₂. However, the factors determining optimized annealing conditions and the mechanism of decreasing the leakage current were still open subjects. In the present work, we have studied the conduction mechanisms of leakage current for as-deposited and post-annealed Ta₂O₅ films prepared by a cold wall-type LPCVD.

Experimental

Experimental apparatus and conditions for film preparation were described in detail in our previous paper (5). Thus, only a brief outline is mentioned here. Ta₂O₅ films were deposited on p-type (100) Si substrates with a resistivity of 3-12 Ω-cm by a cold wall-type LPCVD. We used tantalum ethylate (Ta(OC₂H₅)₅) with 6N purity as a source gas. Ta₂O₅ films were deposited in a reaction chamber made of a quartz tube, and substrates were heated to 400°C by infrared lamps. The typical deposition pressure in the reaction chamber was 0.6 torr. After the deposition, a part of the samples was annealed at 700°-900°C in an atmo-

sphere of O₂ for 30 min. The thickness of films was determined by ellipsometry, and the films with a thickness of 20-40 nm were examined in this experiment.

In order to measure basic electrical characteristics, metal-insulator-semiconductor (MIS) capacitors with an Al gate electrode were prepared. The area of Al gate electrodes was about 5 × 10⁻⁴ cm². On the back side of Si substrates, Al films were evaporated after chemical etching of oxide layers by a diluted HF solution. Post-metallization annealing in N₂ ambient was carried out at 400°C for 30 min. Current-voltage (I-V) characteristics were measured with negative polarity on the Al electrode. The temperature dependence of I-V characteristics was also measured at temperatures ranging from 77 to 300 K.

Results and Discussion

Typical I-V characteristics in MIS capacitors with Ta₂O₅ films for different annealing conditions are shown in Fig. 1, in which the leakage current densities are plotted as a function of a square root of applied electric field. As shown in this figure, the leakage current decreases dras-

Fig. 1. Leakage current density for Ta₂O₅ films as-deposited and annealed at 800°C and 850°C, as a function of the square root of applied electric field at room temperature.

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