## HYDRODYNAMIC DESCRIPTION OF CVD PROCESSES\*

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A CVD process with a two-component gas mixture A–B where only the component B is deposited is solved numerically for an axisymmetric stagnation flow geometry assuming the mass fraction of B on the deposition surface to have a fixed value  $Y_{Bd}$ . A comparison of the calculated flow lines with visualization experiments shows satisfactory agreement. The agreement between calculations and SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> deposition experiments (SiH<sub>4</sub> + O<sub>2</sub>  $\rightarrow$  SiO<sub>2</sub>, SiH<sub>4</sub> + NH<sub>3</sub>  $\rightarrow$  Si<sub>3</sub>N<sub>4</sub>) was good for some deposition ranges. In these ranges the deposition profiles could be calculated with only one fitting parameter ( $Y_{Bd}$ ).

# 1. INTRODUCTION

The complexity of chemical vapor deposition (CVD) processes is caused by the interdependence of the three main stages which determine the deposition: transport of the reactive species to the surface, chemical reaction on or near the surface and transport of the reaction products from the surface.

The theoretical part of this paper describes a simple CVD process in an axisymmetric stagnation flow geometry with the following properties. The gas consists of only two components A and B with mass fractions  $Y_B$  and  $Y_A$ , where  $Y_B \ll Y_A$ ; B is deposited on the sample, which is heated to the deposition temperature  $T_d$ . The thermodynamics and the kinetics of the process may be described by the constant mass fraction  $Y_{Bd}$  as a boundary condition at the deposition surface. This boundary condition can be derived exactly if, for example, the gas phase near the surface is in thermodynamic equilibrium with the deposited material, which has the vapor pressure  $p_B$  of the component B.

The calculations are restricted to laminar and incompressible (Mach number  $Ma \ll 1$ ) flow in the steady state, with the temperature dependence of the gas properties and gravity effects taken into account. Thermodiffusion effects are neglected; this is justified only if A and B have similar molecular weights. Similar calculations have been made<sup>1, 2</sup> for other geometries, but gravity effects and the temperature dependence of the gas properties were not considered in detail.

The results of the theoretical discussion will be compared with the deposition of

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SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> on silicon wafers according to the reactions

$$SiH_4 + O_2 \rightarrow SiO_2 + \dots$$
$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + \dots$$

with nitrogen as the carrier gas. The last part of the paper discusses CVD processes in which an N-component diffusion (N > 2) determines the deposition.

## 2. DEPOSITION GEOMETRY

The deposition calculations and the experiments were performed with the deposition geometry shown in Fig. 1. The reaction gas was led vertically through a nozzle onto a silicon wafer of 2.8 cm diameter. The wafer was attached to a hotplate which was resistance heated at low temperatures and heated by electron bombardment at high temperatures ( $T_d > 700$  K). The deposition temperature  $T_d$  of the silicon plate was variable over the range 300–1300 K and the pressure p in the reaction chamber could be adjusted over the range 10–760 Torr by a valve in the gas outlet. The total gas flow  $i_{tot}$  was varied between 1 and 6 1(STP) min<sup>-1</sup>. The mean gas velocity  $v_0$  in the nozzle can be derived from  $i_{tot}$ :  $v_0 = i_{tot} p_{std}/pA$ , where the standard pressure  $p_{std}$  is 760 Torr and A is the cross section of the nozzle. In our experiments  $v_0$  was in the range 0.1–15 m s<sup>-1</sup>. A more detailed description of the apparatus is given elsewhere<sup>3</sup>.



Fig. 1. Reactor geometry (h heating wire).

The calculations were carried out for the region ABCDEFGH. The geometrical parameters of interest for these calculations are the inner radius  $R_0$  of the nozzle

(0.8 cm), the inner radius  $R_d$  of the deposition chamber (2.8 cm), the radius  $R_{hp}$  of the hotplate (1.6 cm), the distance *d* between nozzle and hotplate (3.0 cm) and the distances AB and FG (Fig. 1) (both 0.4 cm). The thicknesses of the silicon plate (0.035 cm) and of the nozzle wall (0.1 cm) are neglected in the calculations.

## 3. CALCULATIONS FOR A TWO-COMPONENT GAS ( $Y_{\rm B} \ll Y_{\rm A}$ )

The CVD process can be calculated by boundary layer theory<sup>4, 5</sup> as well as by a complete solution of the gas flow problem. The complete solution is no more complicated than the boundary layer problem as the differential equations of both methods are two-dimensional. The second method, however, gives more information<sup>6</sup> than the first and has therefore been chosen to solve our flow problem.

It is thus necessary to solve the following equations 5,7: the continuity equation for the mass,

$$\operatorname{div} \rho \boldsymbol{v} = 0 \tag{1}$$

the continuity equations for the momentum (only the equation for the x direction is given here),

$$\rho v_x \frac{\partial v_x}{\partial x} + \rho v_y \frac{\partial v_x}{\partial y} + \rho v_z \frac{\partial v_x}{\partial z} = -\frac{\partial p}{\partial x} + \rho g n + \frac{\partial}{\partial x} \left\{ \eta \left( 2 \frac{\partial v_x}{\partial x} - \frac{2}{3} \operatorname{div} v \right) \right\} + \frac{\partial}{\partial y} \left\{ \eta \left( \frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) \right\} + \frac{\partial}{\partial z} \left\{ \eta \left( \frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right) \right\}$$
(2)

the continuity equation for the energy,

$$\rho C_{\rm p} v \, {\rm grad} \, T = {\rm div} \, \lambda \, {\rm grad} \, T \tag{3}$$

and the continuity equation for component B,

 $\rho v \operatorname{grad} Y_{\mathrm{B}} = \operatorname{div} \rho D \operatorname{grad} Y_{\mathrm{B}}$  (4)

where x, y, z are cartesian coordinates, v is the barycentric gas velocity with components  $v_x$ ,  $v_y$ ,  $v_z$ ,  $\rho$  is the density, p the pressure, T the temperature,  $\eta$  the viscosity,  $C_p$  the specific heat at constant pressure,  $\lambda$  the heat conductivity, D the binary diffusion coefficient of component B in A, g the acceleration due to gravity and n the unit vector in the direction of g. In addition the perfect gas law

$$\frac{p}{\rho} = \frac{RT}{M} \tag{5}$$

must be fulfilled (R is the gas constant and M the molar mass of the gas).

As the calculations are restricted to incompressible flow (Ma  $\leq 1$ ), the change of the total density due to pressure variations can be neglected, *i.e.* the pressure is assumed to be constant in eqn. (5) so that

$$\frac{\rho}{\rho'} = \frac{T'}{T} \tag{6}$$

where  $\rho$  and  $\rho'$  are the densities at temperatures T and T'. The temperature dependences of  $\eta$ ,  $\lambda$ ,  $C_p$  and D must be considered because of the large temperature differences in CVD processes.

The boundary conditions at the boundaries of the region ABCDEFGH are shown in Fig. 2 (left-hand side). For all the calculations the deposition chamber was assumed to be closed along AB in order to save computation time. The influence of this simplification on the flow and the deposition is negligible. It was assumed that there was no deposition on the cold walls (AB, AH, BC, temperature  $T_0 = 300$  K) and no slip (v = 0) on any wall. In the gas inlet (CD) a Hagen-Poiseuille profile ( $v_z = 2v_0 \{1 - (r/R_0)^2\}$ ) was adopted and in the gas outlet (GH) it was assumed that no axial change of any gas property occurred.



Fig. 2. Boundary conditions in the region ABCDEFGH of Fig. 1. Left, boundary conditions for v, T,  $Y_{\rm B}$ ; right, boundary conditions for  $\omega^*$ ,  $\psi^*$ ,  $\theta^*$ ,  $Y_{\rm B}^*$ ; *n* is the normal to the surface.

It is useful to describe the flow problem by introducing the dimensionless parameters  $x^* = x/R_0$ ,  $y^* = y/R_0$ ,  $z^* = z/R_0$ ,  $v^* = v/v_0$ ,  $\theta^* = (T - T_0)/(T_d - T_0)$ ,  $\rho^* = \rho/\rho_0$ ,  $Y_B^* = (Y_B - Y_{Bd})/(Y_{B_0} - Y_{Bd})$ ,  $p^* = p/\rho_0 v_0^2$ ,  $\lambda^* \circ \lambda/\lambda_0$ ,  $\eta^* \circ \eta/\eta_0$ ,  $C_p^* = C_p/C_{p_0}$ ,  $D^* = D/D_0$ , where  $T_0$ ,  $C_{p_0}$ ,  $\rho_0$ ,  $Y_{B_0}$ ,  $\lambda_0$ ,  $\eta_0$  and  $D_0$  are the gas properties in the plane CD (Fig. 1). In accordance with studies on heat transfer in stagnation flow geometries<sup>5, 8</sup>, the nozzle radius  $R_0$  was taken as the reference length. The gas flow is characterized by the Reynolds number  $\text{Re} (= \rho_0 v_0 R_0/\eta_0)$ , the Prandtl number  $\text{Pr} (= \eta_0 C_{p_0}/\lambda_0)$ , the Schmidt number  $\text{Sc} (= \eta_0/\rho_0 D_0)$ , the Froude number  $\text{Fr} (= v_0^2/gR_0)$ , the temperature quotient  $Q (= T_d/T_0)$  and the temperature dependent parameters  $\eta^*$ ,  $\lambda^*$ ,  $C_p^*$  and  $D^*$ .

The local mass deposition rate  $\dot{m}_{\rm B} (= \rho D \partial Y_{\rm B} / \partial n$  where *n* is the normal to the deposition surface) is described by the Sherwood number Sh  $(= \dot{m}_{\rm B} R_0 / D_0 \rho_0 (Y_{\rm B_0} - Y_{\rm Bd}))$  and

Sh = f(
$$r_s^*$$
, Re, Sc, Pr, Fr,  $Q, \eta^*, \lambda^*, D^*, C_p^*$ ) (7)

where  $r_s^* = r_s/R_0$  ( $r_s$  is the distance from the stagnation point on the deposition

surface). The influence of Pr, Fr,  $\eta^*$ ,  $\lambda^*$ ,  $D^*$  and  $C_p^*$  can be neglected in the isothermal case  $(T_d = T_0)$ :

$$Sh = f(r_s^*, Re, Sc)$$
(8)

The influence of the acceleration g due to gravity on the gas flow, *i.e.* the influence of the Froude number Fr, is only important if there are density variations in the gas. The number which characterizes the competition between forced and free convection is

$$C = \frac{\mathrm{Gr}}{\mathrm{Re}^2} \equiv \frac{1}{\mathrm{Fr}} \frac{\Delta \rho_0}{\rho_0} \tag{9}$$

where Gr is the Grashof number  $(=g\rho_0\Delta\rho_0R_0^3/\eta_0^2)$  and  $\Delta\rho_0$  is a typical density variation in the gas<sup>4, 5</sup>. In order to keep the same reference system the radius  $R_0$  was chosen as the geometric parameter for the definition of the Grashof number. Provided that the density variations are caused by thermal expansion,  $\Delta\rho_0/\rho_0$  can be expressed by  $\Delta\rho_0/\rho_0 = \beta\Delta T_0$  ( $\beta$  is the expansion coefficient) and for an ideal gas by  $\Delta\rho_0/\rho_0 = \Delta T_0/T_0$ , where in our case  $\Delta T_0 = T_d - T_0$ .

The influence of gravity on the gas flow can be neglected if  $Gr/Re^2 < C_0$ , where  $C_0$  is dependent on the geometry and the choice of the geometric parameter. In this paper we have studied the gas flow in the C range 0–22 and our calculations enable us to estimate the value of  $C_0$ . If  $Gr/Re^2 < C_0$  then the deposition is not dependent on Fr, and Sh is given by

Sh = f(
$$r_s^*$$
, Re, Sc, Pr,  $Q, \eta^*, \lambda^*, D^*, C_p^*$ ) (10)

This equation has the interesting feature that all values except Re are pressure independent. Therefore at constant Re the Sherwood number Sh does not depend on pressure and the mass deposition rate

$$\dot{m}_{\rm B} = \frac{D_0 \rho_0}{R_0} (Y_{\rm B_0} - Y_{\rm Bd}) f(r_{\rm s}^*, {\rm Re, Sc, Pr, Q, \eta^*, \lambda^*, D^*, C_{\rm p}^*})$$
(11)

is also pressure independent  $(D_0 \propto 1/\rho_0)$ . The values of  $C_p$ ,  $\lambda$  and  $\eta$  are determined by the gas component A only. As A is usually a common gas like N<sub>2</sub>, Ar or H<sub>2</sub>, these values are known from the literature. The binary diffusion coefficient *D*, however, must be estimated empirically<sup>9</sup>.

For the numerical solution of the gas flow the problem was transformed into cylindrical coordinates. It then depends only on the coordinate z in the direction of the axis and on the radius r. Instead of the velocity components  $v_r$  and  $v_z$ , the stream function  $\psi^*$  defined by

$$\rho^* v_z^* = \frac{1}{r^*} \frac{\partial \psi^*}{\partial r^*} \qquad \rho^* v_r^* = -\frac{1}{r^*} \frac{\partial \psi^*}{\partial z^*}$$

and the vorticity  $\omega^*$ 

$$\omega^* = \frac{\partial v_r^*}{\partial z^*} - \frac{\partial v_z^*}{\partial r^*}$$

were introduced. The resulting equations that have to be solved instead of eqns. (1)–(4) are<sup>6, 10</sup>

$$r^{*2}\left\{\frac{\partial}{\partial z^{*}}\left(\frac{\omega^{*}}{r^{*}}\frac{\partial\psi^{*}}{\partial r^{*}}\right) - \frac{\partial}{\partial r^{*}}\left(\frac{\omega^{*}}{r^{*}}\frac{\partial\psi^{*}}{\partial z^{*}}\right)\right\} = \frac{1}{\operatorname{Re}}\frac{\partial}{\partial z^{*}}\left\{r^{*3}\frac{\partial}{\partial z^{*}}\left(\eta^{*}\frac{\omega^{*}}{r^{*}}\right)\right\} + \frac{1}{\operatorname{Re}}\frac{\partial}{\partial r^{*}}\left\{r^{*3}\frac{\partial}{\partial r^{*}}\left(\frac{\eta^{*}\omega^{*}}{r^{*}}\right)\right\} + \frac{1}{\operatorname{Fr}}r^{*2}\frac{\partial\rho^{*}}{\partial r^{*}} + r^{*2}\left\{\frac{\partial}{\partial z^{*}}\left(\frac{v_{r}^{*2} + v_{z}^{*2}}{2}\right)\frac{\partial\rho^{*}}{\partial r^{*}} - \frac{\partial}{\partial r^{*}}\left(\frac{v_{r}^{*2} + v_{z}^{*2}}{2}\right)\frac{\partial\rho^{*}}{\partial z^{*}}\right\} + r^{*3}S \quad (12)$$

$$\frac{\partial}{\partial z^*} \left( \frac{1}{\rho^* r^*} \frac{\partial}{\partial z^*} \psi^* \right) + \frac{\partial}{\partial r^*} \left( \frac{1}{\rho^* r^*} \frac{\partial}{\partial z^*} \psi^* \right) = -\omega^*$$
(13)

$$C_{\rm p}^* \frac{\partial}{\partial z^*} \left( \theta^* \frac{\partial \psi^*}{\partial r^*} \right) - C_{\rm p}^* \frac{\partial}{\partial r^*} \left( \theta^* \frac{\partial \psi^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) + \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial r^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial r^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial \theta^*}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^* \frac{\partial}{\partial z^*} \right) = \frac{1}{\operatorname{RePr}} \frac{\partial}{\partial z^*} \left( \lambda^* r^*$$

$$\frac{\partial}{\partial z^*} \left( Y_{\mathsf{B}}^* \frac{\partial \psi^*}{\partial r^*} \right) - \frac{\partial}{\partial r^*} \left( Y_{\mathsf{B}}^* \frac{\partial \psi^*}{\partial z^*} \right) =$$
(14)

$$\frac{1}{\operatorname{ReSc}} \frac{\partial}{\partial z^*} \left( \rho^* D^* r^* \frac{\partial}{\partial z^*} Y^* \right) + \frac{1}{\operatorname{ReSc}} \frac{\partial}{\partial r^*} \left( \rho^* D^* r^* \frac{\partial}{\partial r^*} Y_{\mathsf{B}}^* \right)$$
(15)

The term S in eqn. (12) is a rather cumbersome term (given in ref. 6 (eqn. 2.22-47)) and it disappears if  $\eta$  is temperature independent. Following ref. 6 we have neglected S

The equations were solved with the boundary conditions given on the righthand side of Fig. 2, which follow directly from the conditions on the left-hand side and from the given differential equations. For  $\omega^*$  the formula

$$\psi^{*}(n^{*}) = \psi^{*}_{w} - \rho^{*} \left( \frac{r^{*}_{w}}{6} \frac{\partial \omega^{*}}{\partial n^{*}_{w}} n^{*3} + \frac{r^{*}_{w} \omega^{*}_{w}}{2} n^{*2} \right)$$
(16)

was used as the boundary condition at the walls ( $n^*$  is the normal to the surface and the index w denotes the value at the wall). Equation (16) was derived from eqns. (12) and (13) as described in ref. 6. The total boundary value problem was solved numerically by the method of finite differences<sup>6, 10</sup>.

The values  $\psi^*$ ,  $\omega^*$ ,  $Y_B^*$  and  $\theta^*$  were calculated for the nodes of a grid which was formed by 20 equidistant radial lines, including the lines HG, FE, CD and AB in Fig. 1, and by 15 equidistant axial lines, including the lines AH, BC, FG and DE. In addition five more equidistant radial grid lines were outlined between the deposition surface and the first parallel grid line in order to calculate the boundary layer near the deposition surface FE. The iteration procedure was terminated when the condition

$$\frac{\phi_N - \phi_{N-1}}{\phi_{N-1,\max}} < 5 \times 10^{-4} \tag{17}$$

was fulfilled at any node. The abbreviations  $\phi_N$  and  $\phi_{N-1}$  stand for  $\psi^*$ ,  $\omega^*$ ,  $Y_B^*$  and  $\theta^*$  at the Nth and (N-1)th iterations.  $\phi_{N-1,\max}$  is the maximum value of  $\phi$  (*i.e.* of  $\psi^*$ ,

 $\omega^*$ ,  $Y_B^*$ ,  $\theta^*$ ) in the field calculated at the (N-1)th iteration. The computer program was written in FORTRAN IV and normally 100–200 iterations were necessary to reach convergence according to eqn. (17). A typical running time was 100 s on a time-sharing Honeywell Bull Computer Series 60.

### 4. THEORETICAL RESULTS AND VISUALIZATION EXPERIMENTS

The calculations were carried out mostly for an N<sub>2</sub>-SiH<sub>4</sub> mixture ( $Y_{SiH_4} \ll Y_{N_2}$ ). The heat conductivity and the viscosity of N<sub>2</sub> were taken from ref. 11 and the temperature dependence of these values was extrapolated by a straight line on a log-log plot, resulting in

$$\lambda(\text{cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}) = 62 \times 10^{-6} (T/300 \text{ K})^{0.84}$$
  
$$\eta (\text{P}) = 1.8 \times 10^{-4} (T/300 \text{ K})^{0.62}$$

The temperature dependence<sup>12</sup> of the specific heat  $C_p = 0.25$  cal g<sup>-1</sup> K<sup>-1</sup> was neglected. The diffusion coefficient of SiH<sub>4</sub> in N<sub>2</sub>

$$D (\text{cm}^2 \text{ s}^{-1}) = 0.16 (T/300 \text{ K})^{1.7} p^{-1} (\text{atm})^{-1}$$

was derived from the critical temperature and volume of N<sub>2</sub> and SiH<sub>4</sub> using eqns. 11-10 to 11-17 from ref. 9. The resulting Prandtl number Pr and Schmidt number Sc were 0.73 and 0.9 respectively. Figures 3 and 4 show two flow patterns computed for Re = 50 and for different Gr/Re<sup>2</sup> values (Gr/Re<sup>2</sup> = 0 in Fig. 3, Gr/Re<sup>2</sup> = 22 in Fig. 4). The parameters of the flow lines are the values of the reduced flow function  $\psi^* = \psi/v_0 R_0^2 \rho_0$ . The different flow patterns in Figs. 3 and 4 are mainly caused by the different values of Gr/Re<sup>2</sup>. For increasing values of Gr/Re<sup>2</sup> the loop beside the heated cylinder (*i.e.* beside FG in Fig. 1) disappears, whereas the roll under the deposition surface degenerates into a loop reaching into the outlet.



Fig. 3. Calculated flow lines: Re = 50,  $T_d = 300 \text{ K}$ ,  $Gr/Re^2 = 0$  (Fr = 0.09).



Fig. 4. Calculated flow lines: Re = 50,  $T_d = 900$  K,  $Gr/Re^2 = 22$  (Fr = 0.09).



Fig. 5. Calculated flow lines: Re = 50,  $T_d = 900$  K,  $Gr/Re^2 = 22$  (Fr = 0.09).

Figure 5 shows a flow pattern (Re = 50,  $\text{Gr/Re}^2 = 22$ ) in the reverse geometry with the nozzle above the sample. This flow pattern is more complex than that of Fig. 4 because of the influence of gravity. Further flow patterns were calculated for different Re (50 < Re < 250) and different  $\text{Gr/Re}^2$  ( $0 < \text{Gr/Re}^2 < 22$ ). The main parameter which determined the form of the flow patterns was the parameter  $\text{Gr/Re}^2$ . The flow patterns could be divided into two classes. (1) Flow patterns in the form of Fig. 3 were independent of the position of the reactor. In this class gravity has a negligible influence on the gas flow. The number  $\text{Gr/Re}^2$  was always less than of the order of unity. (2) Flow patterns in the form of Figs. 4 or 5 depended on the position of the apparatus. The number  $\text{Gr/Re}^2$  was always greater than of the order of unity. The value of  $C_0 \approx 1$  follows from these considerations.

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Fig. 6. Experimental flow pattern for the flow conditions of Fig. 3. Fig. 7. Experimental flow pattern for the flow conditions of Fig. 4.



Fig. 8. Experimental flow pattern for the flow conditions of Fig. 5.

The calculated patterns are in good agreement with the experimental flow patterns displayed in Figs. 6-8, which were obtained by the  $TiCl_4-H_2O$  method<sup>1</sup>.

The deposition rates, *i.e.* the Sherwood numbers Sh on the deposition surface (EF in Fig. 1), were calculated for different Reynolds' numbers and deposition

temperatures for an  $N_2$ -SiH<sub>4</sub> gas mixture. The number Gr/Re<sup>2</sup> was always less than unity so that we always had a flow pattern like Fig. 3. The Schmidt number was also varied under isothermal conditions.

All calculated Sherwood number profiles on the deposition surface EF had a maximum Sherwood number  $Sh_s$  at the stagnation point. The Sherwood number decreased to approximately  $0.5Sh_s$  on the boundary of the deposition surface (point F in Fig. 1). We found that the profiles could be described approximately by the relation

$$\mathbf{Sh/Sh}_{s} = \mathbf{f}(r_{s}) \tag{18}$$

over the investigated ranges:

- (1) 50 < Re < 250,  $T_{\text{d}} = T_0$ , 0.8 < Sc < 8,  $\text{Gr}/\text{Re}^2 = 0$
- (2)  $50 < \text{Re} < 250, 300 \text{ K} < T_{d} < 1300 \text{ K}, \text{N}_{2}-\text{SiH}_{4} \text{ mixture, Gr/Re}^{2} < 1$

The function  $f(r_s)$  is shown in Figs. 9 and 10.



Fig. 9. Theoretical and experimental profiles for the silicon wafers 1-4 (see Fig. 11): s is the local thickness,  $s_s$  the thickness at the stagnation point and  $r_s$  the distance from the deposition surface to the stagnation point.

Fig. 10. Theoretical and experimental profiles for silicon wafers 1-3 (see Fig. 12).

In the isothermal case the following relation was found for the Sherwood number  $Sh_s$  at the stagnation point:

$$Sh_s = \alpha Sc^{1/3} Re_{max}^{1/2} \qquad \alpha = 0.65 \pm 0.02$$
 (19)

where the Reynolds number  $\text{Re}_{max}$  is calculated for the maximum velocity  $v_{max}$  in the nozzle. Since in the case of a Hagen–Poiseuille profile the relation  $v_{max} = 2v_0$  is fulfilled, the Reynolds number  $\text{Re}_{max}$  is related to Re by  $\text{Re}_{max} = 2 \text{ Re}$ . Equation (19) is in good agreement with boundary layer approximations for a gas flowing perpendicularly with velocity  $v_{max}$  towards an infinite circular plate. For this flow the same dependence on Sc and Re was found<sup>4, 8, 13</sup> with the factor  $\alpha = 0.55$ . In refs. 4 and 8 these boundary layer approximations were made for the heat transfer. The relations obtained there can be transformed into mass transfer relations by

replacing the Nusselt number Nu and the Prandtl number Pr by Sh and Sc (heat-mass transfer analogy).

For the non-isothermal case the temperature dependence of the Sherwood number  $Sh_s$  can be described by

$$Sh_s = 14.0 \left(T_d / 300 \text{ K}\right)^{0.4}$$
(20)

for an N<sub>2</sub>-SiH<sub>4</sub> gas mixture (Sc = 0.9, Pr = 0.73, 50 < Re < 250 with Gr/Re<sup>2</sup> < 1). For these Gr/Re<sup>2</sup> values Sh does not depend on gravity (deviation < 5%), as was confirmed by calculation.

#### 5. CVD EXPERIMENTS

For the theoretical calculation of the CVD reactions

$$3\mathrm{SiH}_4 + 4\mathrm{NH}_3 \rightarrow \mathrm{Si}_3\mathrm{N}_4 + \dots$$

 $SiH_4 + O_2 \rightarrow SiO_2 + \dots$ 

it is assumed that during deposition a constant SiH<sub>4</sub> mass fraction  $Y_d(SiH_4)$  is maintained on the deposition surface. Since NH<sub>3</sub> (O<sub>2</sub>) is in excess in the reactive gas mixture, the deposition is determined by the SiH<sub>4</sub> diffusion to the surface. In thermodynamic equilibrium the SiH<sub>4</sub> partial pressure on SiO<sub>2</sub> (Si<sub>3</sub>N<sub>4</sub>) is small  $(p_{SiH_4} \ll 10^{-10} \text{ Torr})^{12}$  so that  $Y_d(SiH_4) = 0$  would be justified, but because we are not sure that this equilibrium is reached we use the above boundary condition that  $Y_d$  is a constant greater than or equal to zero. An estimate according to the Wilke method<sup>9, 14</sup> shows that SiH<sub>4</sub> diffusion can be described by the binary diffusion coefficient *D* of SiH<sub>4</sub> in N<sub>2</sub>. In our case the N<sub>2</sub> data<sup>11, 12</sup> for  $\lambda$ ,  $\eta$  and  $C_p$  can be used. Therefore the considerations of Section 4 can be applied, leading to the Sherwood numbers Sh for the mass transport of SiH<sub>4</sub> to the surface. All SiH<sub>4</sub> transferred to the surface is assumed to react to Si<sub>3</sub>N<sub>4</sub> (SiO<sub>2</sub>). Thus it is possible to calculate the deposition rate of Si<sub>3</sub>N<sub>4</sub> (SiO<sub>2</sub>) from the transfer of SiH<sub>4</sub> to the surface.

The CVD experiments were carried out with the geometry shown in Fig. 1, the deposition surface being above the nozzle. During the deposition of SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> onto the silicon wafers the thickness growth rates  $\dot{s}_s$  at the stagnation point were measured automatically by monitoring the interference maxima of a monochromatic light source ( $\lambda = 4050$  Å) with a photocell. All measurements showed the thickness to be proportional to the deposition time. After deposition the profiles were measured by observation of the interference colors.

The  $Si_3N_4$  deposition was made under the following conditions:

 $Y_0(\text{SiH}_4) = 0.0021$   $Y_0(\text{NH}_3) = 0.02$   $Y_0(\text{Ar}) = 0.026$ total gas flow  $i_{\text{tot}} = 5.12$  1(STP) min<sup>-1</sup> (Re = 250) 950 K <  $T_d$  < 1100 K (Gr/Re<sup>2</sup> < 1) 100 Torr < p < 760 Torr

Ar is the dilution gas of commercial  $SiH_4$ . Figure 11 shows the measured deposition rates  $\dot{s}_s$  at the stagnation point for different pressures and temperatures. In addition

the theoretical lines (calculated with the help of eqn. (20)) are displayed in Fig. 11 with the deposition temperature and the quotient

$$y = \frac{Y_0(\text{SiH}_4) - Y_d(\text{SiH}_4)}{Y_0(\text{SiH}_4)}$$
(21)

as parameters, where  $\gamma$  has the maximum value  $\gamma = 1$ , when  $Y_d(\text{SiH}_4) = 0$ . These lines are pressure independent because gravity can be neglected (see eqn. (11)). The  $\gamma$  values which fit the measured deposition rates are given at each measuring point. These  $\gamma$  are pressure and temperature dependent. The maximum value reached is  $\gamma = 0.5$ .

The deposition profiles of the wafers 1–4 are shown in Fig. 9. Similar good agreement was found for the wafers whose measuring points are marked by squares in Fig. 11. Further profiles produced under the deposition conditions p = 1 atm,  $i_{tot} = 5.12 \ \text{I(STP)} \ \text{min}^{-1}$ ,  $T_d = 1100 \ \text{K}$  or 1050 K with various  $Y_0(\text{NH}_3)$  (0.01 <  $Y_0(\text{NH}_3) < 0.078$ ) were measured and they again agreed with the predicted curve. At low temperatures the profiles became irregular but they always showed a maximum at the stagnation point. These irregularities are probably caused by the very strong temperature dependence of the deposition rate in this deposition range. Small changes in surface temperature can produce a change in deposition rate. The measuring points of the wafers with these irregular profiles are marked by circles in Fig. 11.



Fig. 11. Theoretical and experimental thickness growth rates  $\hat{s}_s$  of  $Si_3N_4$  at the stagnation point *vs.* the pressure p: —— theoretical growth rate (parameters  $\gamma$  and  $T_d$ );  $\blacksquare$  the measured profile is in accordance with the calculated profile;  $\bullet$  the measured profile disagrees with the calculated profile. Parameters at the measuring points: (1) the number of the wafer (only given at some points); (2) the  $\gamma$  value that is used to fit the experimental value to the theory.

Fig. 12. Theoretical and experimental thickness growth rates  $\hat{s}_s$  of SiO<sub>2</sub> at the stagnation point *vs.* the pressure p: —— theoretical growth rate (parameters  $\gamma$  and  $T_d$ );  $\blacksquare$  the measured profile agrees with the calculated profile;  $\times$  the profile is flatter than the theoretical profile;  $\blacklozenge$  crater profile;  $\downarrow$  no deposition was measured.

Figure 12 shows the results of the  $SiO_2$  deposition with the following deposition conditions:

 $Y_0(\text{SiH}_4) = 0.0021$   $Y_0(\text{O}_2) = 0.074$   $Y_0(\text{Ar}) = 0.051$ total gas flow  $i_{\text{tot}} = 5.12 \ 1(\text{STP}) \ \text{min}^{-1}$  (Re = 250) 750 K <  $T_d$  < 1000 K (Gr/Re<sup>2</sup> < 1) 20 Torr < p < 760 Torr

The theoretical lines for different  $T_d$  and  $\gamma$  are also shown and some  $\gamma$  values found by fits of the experimental data to the theory are given. All these  $\gamma$  values lie below 0.25.

For wafers 1–3 (Fig. 12) the deposition profiles were measured and compared with the theoretical curve as shown in Fig. 10. Again good agreement with the theory was found for all layers produced with the deposition conditions 100 Torr  $Torr, 900 K <math>< T_d < 1000$  K. The measuring points of these wafers are marked by squares in Fig. 12. With decreasing temperature or decreasing pressure the profiles become flatter and finally degenerate to a crater profile with a minimum deposition rate at the stagnation point. The measuring points on the wafers with minimum profiles are marked by circles in Fig. 12.

All these measurements show that the CVD processes studied have deposition ranges over which the deposition profiles agree with the calculations. For absolute values of the deposition rates only one fitting parameter ( $\gamma$ ) is necessary for each profile. This parameter must be deduced from Figs. 11 and 12. There are ranges, however, where our model is not applicable (*e.g.* in the case of SiO<sub>2</sub> for p < 100 Torr or  $T_d < 900$  K). In these ranges more complicated boundary conditions may be necessary for calculating the deposition profiles.

## 6. CVD PROCESSES IN *N*-COMPONENT GASES (N > 2)

A difficulty in simulating CVD processes in real multicomponent gases is that instead of the Fick law (diffusion proportional to the concentration gradient) the Stefan–Maxwell equations<sup>15</sup> must be used to describe the relation between the diffusion gas flows and the concentration gradients.

There are three ways of solving this problem:

(1) by an exact numerical computation;

(2) by an approximate calculation using the Wilke method<sup>14</sup> which enables us to describe the diffusion by a Fick law with concentration-dependent diffusion coefficients; and

(3) by an empirical estimation as in the Carlton–Oxley model<sup>16</sup>. In this model the boundary layer thickness is calculated from CVD processes in two-component gases where only one component is deposited. The Stefan–Maxwell equations must be solved in this boundary layer in order to obtain the deposition rate.

The first method of solving this problem is described in ref. 17 but it was not applied to CVD processes. The second method has been applied<sup>10</sup> to the deposition of metals from halogenides. The third method has been used<sup>13</sup> for calculating the deposition of W (WF<sub>6</sub> + 3H<sub>2</sub>  $\rightarrow$  W + 6HF) at the stagnation point. This method has the advantage that the theoretical results of two-component CVD processes (as described in this paper) are applicable.

## 7. CONCLUSIONS

CVD processes can be calculated by hydrodynamic methods as described in this paper. These methods can also be employed for the calculation of deposition on samples of a complicated shape. The advantage of this method is that deposition rates can be predicted and optimal deposition parameters can be chosen. Computer simulation is useful for the application of CVD. A comparison of computations and experimental data should allow the selection of those processes which result in deposition.

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### REFERENCES

- 1 R. Takahashi, Y. Koga and K. Sugawara, J. Electrochem. Soc., 119 (1972) 1406.
- 2 K. Sugawara, J. Electrochem. Soc., 119 (1972) 1749.
- 3 G. Wahl, in J. M. Blocher, H. E. Hintermann and L. H. Hall (eds.), Proc. 5th Int. Conf. on CVD, 1975, The Electrochemical Society, Princeton, N.J., 1975, p. 391.
- 4 H. Schlichting, Grenzschichttheorie, G. Braun, Karlsruhe, 1965.
- 5 H. Brauer, Stoffaustausch, Sauerländer, Frankfurt, 1971.
- 6 A. D. Gosman, W. M. Pun, A. K. Runchal, D. B. Spalding and M. Wolfshtein, *Heat and Mass Transfer in Recirculating Flows*, Academic Press, London, 1973.
- 7 K. Oswatitsch, in S. Flügge (ed.), *Physikalische Grundlagen der Strömungslehre*, Handbuch der *Physik*, Vol. VIII/1, Springer, Berlin, 1959.
- 8 S. P. Kezios, Heat transfer on the flow of a cylindrical air jet normal to an infinite plane, *Ph.D. Thesis*, Illinois Institute of Technology, Chicago, 1956.
- 9 R. C. Reid and Th. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1958.
- 10 J. E. Mazille, Étude et résolution numérique d'un problème d'aerothermochimie, *Thesis*, Grenoble, 1973.
- R. C. Weast, S. M. Selby and C. D. Hodgman (eds.), Handbook of Chemistry and Physics, 46th edn., Chemical Rubber Co., Cleveland, Ohio, 1965–1966.
- 12 D. R. Stull and H. Prophet (eds.), JANAF Thermochemical Tables, 2nd edn., Natl Stand. Ref. Data Ser., Natl. Bur. Stand., 37, 1971.
- 13 G. Wahl and P. Batzies, in G. F. Wakefield and J. M. Blocher (eds.), *Proc. 4th Int. Conf. on CVD*, 1973, The Electrochemical Society, Princeton, N.J., 1973, p. 425.
- 14 C. R. Wilke, Chem. Eng. Prog., 46 (1950) 95.
- 15 R. B. Bird, W. E. Stewart and E. N. Lightfoot, Transport Phenomena, Wiley, New York, 1960.
- 16 H. E. Carlton and J. H. Oxley, in A. C. Schaffhauser (ed.), Proc. on CVD of Refractory Metals, Alloys and Compounds, Gatlinburg, 1967, Am. Nuclear Society, Hinsdale, Ill., 1967, p. 19.
- 17 R. A. Graff and P. N. Walsh, Chem. Eng. Prog. Symp. Ser., 63 (1967) 70.