

General and Inorganic Chemistry

Mathematical simulation of gas-phase deposition of epitaxial silicon films in the Si—C—H and Si—H systems

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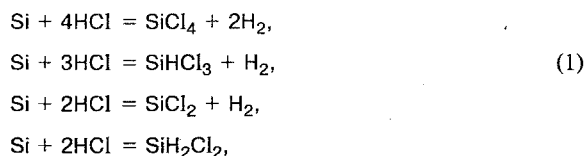
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The effect of experimental conditions on the magnitude and uniformity of the deposition rate of epitaxial silicon obtained by chemical deposition from the gas phase in the $\text{SiCl}_4\text{—H}_2$, $\text{SiHCl}_3\text{—H}_2$, and $\text{SiH}_4\text{—H}_2$ systems (in the temperature ranges from 1300 to 1520 K for the chloride and 1270 to 1370 K for the silane systems) has been examined. Chloride and silane processes are compared.

Key words: deposition rate, surface, silane, silicon, chlorosilanes, flow rate of the vapor-gas mixture, channel.

Heat and mass transfer in the process of epitaxial deposition of silicon in the reactor whose scheme is presented in Fig. 1 has been studied. The reactor is a horizontal channel of rectangular cross section. The surface of the substrate-holder is heated to the temperature of deposition, which is considerably higher than the temperature of the cooled walls of the reactor. The temperature of the heater is maintained at 1300 to 1550 K. Hydrogen is used as a carrier gas. The process can be performed both at atmospheric and reduced pressures.

Taking into account the components, which are formed as products of heterogeneous reactions on the deposition surface in the $\text{SiCl}_4\text{—H}_2$ and $\text{SiHCl}_3\text{—H}_2$ systems, the following reactions are possible for the chloride processes:



and the silane process is characterized by the reaction



When the ratio of the channel width to its height $\gg 1$, the effect of side walls can be neglected. In this

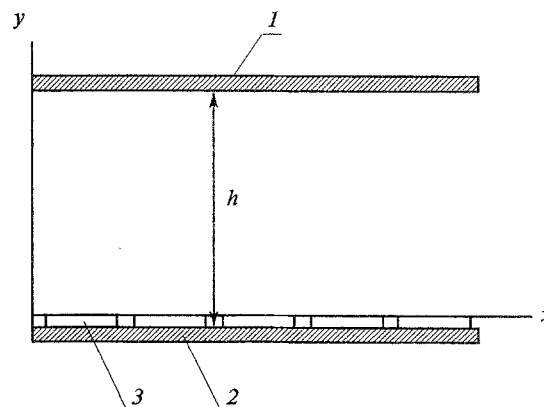


Fig. 1. Scheme of the reactor: 1, cooled wall; 2, base; and 3, substrates.

case when the flow rate of the gas mixture is rather high (the Reynolds criterion $Re > 100$) and the free convection can be neglected, the heat and mass transfer in the reactor can be described by differential equations of conservation in the approximation of the boundary layer:

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0, \quad (3)$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{dP}{dx} + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right), \quad (4)$$

$$\rho u \frac{\partial H}{\partial x} + \rho v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y} \left(\frac{\lambda}{C_p} \cdot \frac{\partial H}{\partial y} \right), \quad (5)$$

$$\rho u \frac{\partial C_i}{\partial x} + \rho v \frac{\partial C_i}{\partial y} = \frac{\partial}{\partial y} \left[\rho D_i \left(\frac{\partial C_i}{\partial y} + \frac{\alpha_T C_i}{T} \frac{\partial T}{\partial y} \right) \right], \quad (6)$$

where x and y are longitudinal and lateral coordinates; u and v are longitudinal and lateral components of the flow rate of the gas mixture; C_i is the weight concentration of the i th component; D_i is the diffusion coefficient of the i th component; H is enthalpy; ρ is the density of the vapor-gas mixture; T is temperature; α_T is the thermal diffusion ratio; λ is the heat conductivity of the vapor-gas mixture; C_p is the heat capacity coefficient; and P is pressure. The index i denotes the following components of the mixture: 1, H_2 ; 2, $SiCl_4$ (SiH_4); 3, HCl ; 4, $SiCl_2$; 5, $SiHCl_3$; and 6, SiH_2Cl_2 .

Uniform profiles of the rate, temperature, and concentrations of initial substances are specified at the input of the channel. The temperature of the walls of the channel is maintained constant at each point. The system of Eqs. (3)–(6) was solved under the following boundary conditions*:

(1) at the input of the channel

at $x = 0$, $u = u_0$, $v = v_0$, $T = T_0$;

for $SiCl_4$ $C_1 = C_{01}$, $C_2 = C_{02}$,
 $C_{03} = C_{04} = C_{05} = C_{06} = 0$;

for $SiHCl_3$ $C_1 = C_{01}$, $C_5 = C_{05}$,
 $C_{02} = C_{03} = C_{04} = C_{06} = 0$;

for SiH_4 $C_1 = C_{01}$, $C_2 = C_{02}$;

(2) on the deposition surface

$u = v = 0$, $T = T_s$,

for the silane process $C_2 = 0$

for the chloride process

$$K_1 = \frac{X_1^2 X_2}{P_0 X_3^4}, K_2 = \frac{X_1 X_5}{P_0 X_3^3}, K_3 = \frac{X_1 X_4}{X_3^2}, K_4 = \frac{X_6}{P_0 X_3^2};$$

for $SiCl_4-H_2$

$$\varphi = \frac{4X_2 + X_3 + 2X_4 + 3X_5 + 2X_6}{2X_1 + X_3 + X_5 + 2X_6} = \frac{4X_{02}}{2X_{01}}, \quad (7a)$$

for $SiHCl_3-H_2$

$$\varphi = \frac{4X_2 + X_3 + 2X_4 + 3X_5 + 2X_6}{2X_1 + X_3 + X_5 + 2X_6} = \frac{3X_{05}}{2X_{01}}, \quad (7b)$$

$$\sum_{i=1}^6 X_i = 1,$$

X_i is the molar concentration of the i th component;
(3) on the cooled wall

$$u = v = 0, \quad T = T_w, \quad \frac{\partial C_i}{\partial y} + \frac{\alpha_T C_i}{T} \frac{\partial T}{\partial y} = 0, \quad i = 1, 6.$$

The value of φ is determined as the ratio of the number of chlorine molecules to the number of hydrogen molecules (7a, 7b) and has a fixed magnitude, because the components considered are not consumed to the formation of silicon. The equilibrium constants are determined from the expression

$$K = \exp \left(\frac{\Delta S}{R} - \frac{\Delta H}{RT} \right)$$

(R is the universal gas constant and S is entropy), according to the data presented in Table 1.

Since the concentration of the initial reagent in the gas mixture is low, the thermal effect of chemical reactions can be neglected. The temperature dependences of the rates of considered chemical reactions^{2–5} allow one to assume that the deposition can be considered as the heterogeneous process, which occurs in the diffusion region.

The system of Eqs. (3)–(6) described above with the boundary conditions is solved numerically by the implicit finite difference method.⁶ The physical properties of the vapor-gas mixture (density, viscosity, thermal conductivity, thermal capacity, and diffusion coefficients), which enter Eqs. (3)–(6), are considered to depend on temperature, pressure, and chemical composition.

The dynamic viscosity coefficient is calculated by Sutherland's formula:⁷

$$\mu_i = \mu_{0i} \frac{273 + C_{s_i}}{T + C_{s_i}} \left(\frac{T}{273} \right)^{1.5},$$

where μ_{0i} is the dynamic viscosity coefficient of the i th component at 0 °C and C_s is the Sutherland constant of

Table 1. Thermodynamic parameters of the multi-component mixture¹

Component	ΔH_{298} kJ mol ⁻¹	ΔS_{298} e.u.	$C_p = A + BT \cdot 10^{-3} + CT^2 \cdot 10^{-5}$		
			A	B	C
H ₂	0.0	31.21	6.52	0.78	0.12
Si	0.0	4.50	5.7	0.7	-1.04
HCl	-22.06	44.62	6.34	1.1	0.26
SiCl ₄	-156.7	79.01	25.39	0.23	-3.51
SiHCl ₃	-116.9	74.85	22.79	1.43	-4.76
SiH ₂ Cl ₂	-75.0	68.47	20.34	2.58	-5.86
SiCl ₂	-38.2	67.4	13.62	0.22	-1.26

* The indices s, w, and 0 relate to the values on the deposition surface (s), on the cooled wall (w), and at the input of the reactor (0).

the i th component:

	H ₂	SiCl ₄	SiH ₄	HCl	SiCl ₂	SiHCl ₃	SiH ₂ Cl ₂
C _s	84.4	486	155	362	1001	143.5	386

Viscosity of the gas mixture is determined by Wilk's formula⁸

$$\mu_m = \sum_{i=1}^6 \frac{\mu_i}{1 + \frac{1}{X_i} \sum \Phi_{ij} X_j},$$

where Φ_{ij} is the function of viscosity and molecular masses of individual components

$$\Phi_{ij} = \frac{\left(1 + (\mu_i/\mu_j)^{0.5} (M_j/M_i)^{0.25}\right)^2}{8 \left(1 + M_i/M_j\right)^{0.5}},$$

where M_i is the molecular mass of the i th component.

By analogy to viscosity, diffusion coefficients of the binary systems are calculated by Sutherland's formula

$$D_{ij} = D_{ij}^0 \frac{273 + C_{sij}}{T + C_{sij}} \left(\frac{T}{273}\right)^{2.5},$$

where D_{ij}^0 is the diffusion coefficient of the i th component at 0 °C. To calculate diffusion coefficients of the multi-component system, Wilk's formula, which gives acute results, is used

$$D_i = \frac{1 - X_i}{\sum_{j \neq i} \frac{X_j}{D_{ij}}},$$

where X_i and X_j are the molar fractions of components in the gas mixture.

The thermal diffusion ratio α_T is a function of temperature and is described by the expression⁹

$$\alpha_T = \alpha_i(1 - T_i'/T). \quad (8)$$

The temperature restriction is described by the corresponding formula for gases ($\Gamma_i > 0$)

$$\alpha_i = (0.425\Delta_i + 0.125)(\Gamma_i + 0.25) - 0.138,$$

$$\Gamma_i = \frac{M_i - M_H}{M_i + M_H}$$

(M_H is the molecular mass of the carrier gas, i.e., hydrogen).

The ratio of the encounters of the opposite cross-sections is determined as

$$\Delta_i = \frac{\sigma_{ij}^2 I_{\mu ij}}{\sigma_{jj}^2 I_{\mu jj}} \quad \text{and} \quad I_{\mu ij} = 1.22 \left(\frac{\varepsilon_{ij}}{kT}\right)^{0.16},$$

where σ_{ij} is the encounter diameter of molecules; I_{μ} is the encounter integral for viscosity, which depends on ε_{ij}/kT ; ε_{ij} is the energy of molecular interaction; and k is

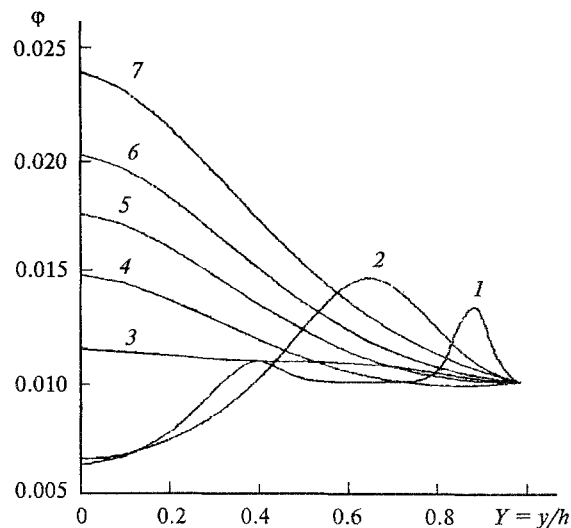


Fig. 2. Distribution of ϕ over the cross section of the channel for the SiCl₄—H₂ system. $T_0 = 298$ K, $T_w = 673$ K, $T_s = 1473$ K, $P = 10^6$ kPa, the flow rate of the vapor-gas mixture $G = 5$ m³ h⁻¹. x/cm : 0.1 (1); 1.5 (2); 6.5 (3); 14 (4); 21.7 (5); 30 (6); 40 (7).

the Boltzman constant. The temperature parameter T_i entering Eq. (8) for the thermal diffusion coefficient, where hydrogen is the carrier gas, is calculated by the previously described method.¹⁰

Let us consider the effect of conditions of the process on the rate of silicon deposition. The rate distribution of silicon deposition over the length of the reactor depends on many factors, main of which are the chemical composition, the flow rate and temperature of the vapor-gas mixture, and the structure and geometrical size of the reactor. The effect of these factors is complex. The extent of the effect of each of them depends on the combination of all of the others. The dependences of the rate distribution of silicon deposition over the length of the reactor on different factors in the SiCl₄—H₂, SiHCl₃—H₂, and SiH₄—H₂ systems have been obtained by the numerical study.

When the flow moves along the reaction zone, the profile ϕ changes continuously, and its maximum moves toward the cooled wall (Fig. 2). The ϕ value on the surface of the pedestal differs considerably from that in the main flow due to a strong difference in diffusion coefficients of components considered.

The analysis of the change in composition of the vapor-gas mixture during its flowing along the reaction zone (Fig. 3) allows one to make a conclusion that initial chlorosilane (SiCl₄ or SiHCl₃) and HCl are the main components of the flow. In the regimes considered, the output of initial chlorosilane does not exceed 70 %, and the content of hydrogen chloride at the outlet of the reactor is comparable to that of initial chlorosilane (Fig. 3).

Comparison of the growth rates obtained by calculation in the binary mixture approximation and for the

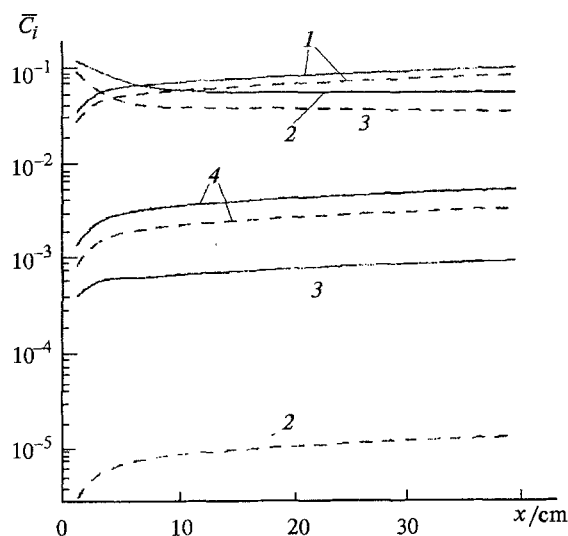


Fig. 3. Change in the average mixed weight composition of the vapor-gas mixture along the channel (for conditions see Fig. 2). The $\text{SiCl}_4\text{--H}_2$ system is indicated by the solid line; the $\text{SiHCl}_3\text{--H}_2$ system is shown by the dashed line. 1, HCl ; 2, SiCl_4 ; 3, SiCl_2 ; 4, SiHCl_3 .

model of the multi-component mixture indicates that the process can be calculated in the binary mixture approximation (the concentration of the initial chlorosilane on the surface of deposition is equal to zero) only at low concentrations of initial chlorosilane in the mixture ($X_{02} < 0.3\%$).

For the accepted diffusion model of boundary layer, no noticeable effect of pressure in the reactor and temperature of the surface of deposition on the growth rate is found, which agrees with the experimental data.^{11,12} The thermodynamic calculation shows that a change in the pressure and the temperature of the boundary layer (T_b) at the fixed initial composition of the mixture results in a sharp change in equilibrium molar ratios of the components (SiH_2Cl_2 , SiCl_2), which exert no noticeable effect on the growth rate. As for initial chlorosilane (SiCl_4 or SiHCl_3) and SiH_4 , its partial pressure on the surface of deposition at the input molar fractions considered (0.001 to 0.05) is so low that its change is also inappreciable.

Let us introduce the following parameter

$$\eta = \frac{v_{\max} - v_{\min}}{v_{\max} + v_{\min}} \cdot 100\%,$$

as a quantitative parameter of the deposition rate distribution. Here v is the rate of deposition of the layer formed. The parameter η is numerically equal to the maximum deviation from the mean value of the deposition rate.

It is of interest to compare silane and chloride processes. Figures 4 and 5 show the growth rate distribution over the length of the channel for tetrachloride, trichlorosilane, and silane processes calculated under similar conditions. The values of growth rates for the

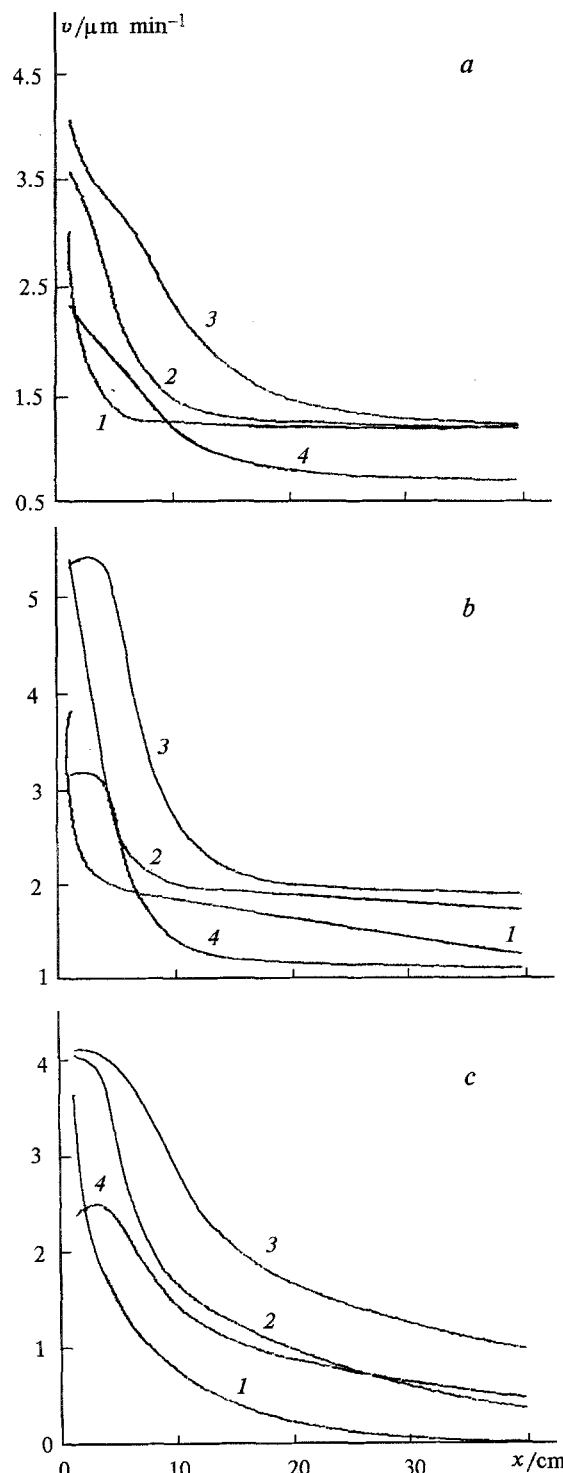


Fig. 4. Effect of the flow rate of the vapor-gas mixture and the height of the channel on the distribution of the rate of silicon deposition (for conditions see Fig. 2). a, $\text{SiCl}_4\text{--H}_2$; b, $\text{SiHCl}_3\text{--H}_2$; c, $\text{SiH}_4\text{--H}_2$. $G/\text{m}^3 \text{ h}^{-1}$: 2 (1), 5 (2, 4), 10 (3); the length of the channel h/cm : 1.5 (1–3), 2.5 (4).

silane process are much higher due to a higher value of the diffusion coefficient. However, the nonuniformity over the length is higher for the silane process ($\eta_2 =$

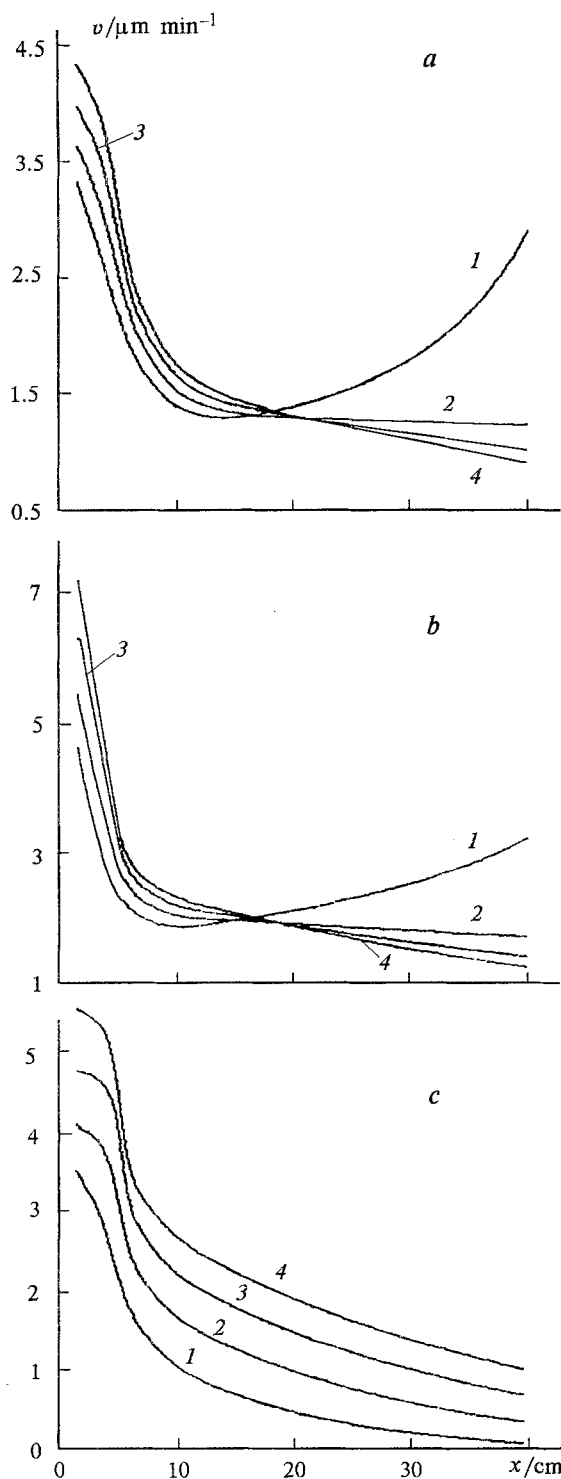


Fig. 5. Effect of the cooled wall temperature T_w on the distribution of the rate of silicon deposition (for conditions see Figs. 2 and 4). T_w (K) = 473 (1), 673 (2), 873 (3), 1073 (4).

62.5 %, Fig. 4, c) than for chloride processes ($\eta_2 = 9$ %, Fig. 4, a; $\eta_2 = 7$ %, Fig. 4, b) over a length of 10 to 400 mm. The output of silane is more intense for the silane process. For example, for the regimes shown in Fig. 4 (curves 2) the output of SiH_4 is 91 % over a

length of 400 mm, while it is 60 % for SiCl_4 and 71 % for SiHCl_3 . The deposition rate is proportional to the mass concentration of silanes introduced at the input of the reactor, and the uniformity over the length of the channel remains nearly unchanged.

For the same geometry of the reaction zone, the deposition rate distribution depends on the flow rate of the vapor-gas mixture. Figure 4 shows that a decrease in the flow rate of the mixture results in a decrease in the deposition rate and in a drop in the concentration of initial silane at the outlet of the reactor, i.e., the extent of using the reagents increases; the uniformity of the growth rate increases over the length of the channel for the chloride CVD-process ($\eta_1 = 0.4$ %, $\eta_3 = 30$ %, Fig. 4, a) and decreases for the silane process ($\eta_1 = 95$ %, $\eta_3 = 47$ %, Fig. 4, c). Thus, in chloride CVD-processes, large outputs do not provide the necessary uniformity of the growing layer and decrease the extent of using initial reagents.

The effect of the character of cooling the external wall of the reactor on the rate of deposition of silicon films is not less than that of the value of the flow rate of gas (Fig. 5). In the case of low temperatures of the cooled wall, T_w , the reaction occurs in the region close to the surface of deposition. An increase in the deposition rate as T_w increases is explained by the fact that higher values of diffusion coefficients of initial components provide an increase in the mass flow toward the surface of deposition due to the greater heating of the reactor. For the silane process, an increase in the temperature of the cooled surface causes the growth of the deposition rate and the enhancement of the uniformity of distribution of the growing layer ($\eta_1 = 80$ %, $\eta_4 = 43$ %, Fig. 5, c). In the case of chloride processes, an increase in the temperature of the cooled surface decreases the uniformity of distribution of the growing silicon layer ($\eta_2 = 9$ %, $\eta_4 = 30$ %, Fig. 5, a; $\eta_2 = 7$ %, $\eta_4 = 28$ %, Fig. 5, b).

The effect of the temperature of the vapor-gas mixture at the input of the channel is noticeable only in the initial region of the channel. The uniformity of distribution of the silicon deposition rate slightly depends on this temperature. An increase in the height of the channel results in a decrease in the silicon deposition rate and the output of initial reagents as well as in a decrease in the uniformity of distribution of the depositing layer over a length of the reaction zone (Fig. 4).

The calculations have revealed the effect of various technological and structural parameters on the value of the rate of deposition of monocrystalline silicon films and its distribution over the length of the channel. The comparative analysis of silane and chloride processes shows that deposition rates are considerably higher for the silane process, and the uniformity of their distribution over the length of the channel are substantially lower due to the intense output of silane.

An increase in the initial concentration of the initial reagent results in increase in the deposition rate. The

calculations of heat and mass transfer processes can be performed in the binary mixture approximation for low initial concentrations of chlorosilanes in the mixture ($X_{02} \leq 3\%$). The uniformity of the deposition rate distribution over the length of the channel depends on the flow rate of the vapor-gas mixture: it decreases for the silane process and increases for the chloride process as the flow rate increases, and absolute values of deposition rates increase.

A decrease in the temperature of the cooled surface of the reaction zone results in a decrease in the deposition rate; for the silane process it enhances and for chloride processes it degrades the uniformity of the deposition rate distribution over the length of the reaction zone. The temperature of the mixture at the input exerts an effect only in some initial region of the pedestal; a decrease in this temperature results in the decrease in the deposition rate. For the diffusion model accepted, the temperature of the base and pressure in the reactor exert nearly no effect on absolute values of deposition rates and their distribution over the length of the channel. Thus, the distribution of deposition rates over the length of the pedestal and their absolute values are determined by the combination of technological parameters of the process and geometrical sizes of the reactor.

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