dioxide gas in liquid n-heptane at a pressure below the condensation pressure the transition of carbon dioxide from the gaseous into the liquid state occurs; 2) for carbon dioxide concentrations in the mixture that exceed 70%, a two-phase system consisting of solid carbon dioxide and liquid n-heptane, whose molecule translational motions are retarded, exists in the temperature domain below the melting point of solid $CO_2$.

## NOTATION

T, absolute temperature; $^{13}C$, carbon isotope; D, coefficient of translational self-diffusion of molecules; $T_1$, nuclear magnetic spin-lattice relaxation time; $n_{cd}$, carbon dioxide concentration in the solution; $m_{cd}$, $P_{cd}$, mass and pressure of the saturated carbon dioxide vapors.

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# APPROXIMATE MODEL OF THE DEPOSITION OF THIN FILMS FROM VAPOR-GAS PHASE IN A TUBULAR DIFFUSION FURNACE

G. I. Georgiev, S. G. Karbanov,
and G. A. Peev

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The analytical conditions for obtaining uniform films deposited from vapor-gas phase in a laminar-isothermal flow are determined.

The deposition of thin dielectric and semiconductor films from the gas phase as a result of heterogeneous chemical reactions is widely used in microelectronics. Cylindrical reactors with vertical substrates (silicon plates) transverse to the flow are often used for this purpose (Fig. 1). In describing the processes in such reactor, it is usually assumed [1, 2] that the longitudinal flow of the gas mixture between the bundle of plates and the reactor wall is isothermal and laminar; that the gas phase between the plates is motionless and transfer of the active component to their surface is on account of molecular diffusion; and that chemical reaction at the plate surface is of first or higher order with respect to the concentration of the active component, which remains constant around the plate over the length of the reactor.

In these conditions, the process is described [1] by the differential equation

$$\frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial z^2} = 0 \tag{1}$$

with the boundary conditions

$$r = R, \ C(r, z) = C(R, z) = C_0; \tag{a}$$

$$r = 0, \ \frac{\partial C}{\partial r} = 0; \tag{b}$$

$$z = 0, \ z = H, \ \left| D \frac{\partial C}{\partial z} \right| = KC^{\alpha}. \tag{c}$$

This problem is solved by the numerical methods of [1]. It was solved analytically in [2], introducing the constraint that the chemical process is of first order, i.e., $\alpha = 1$. The solution is written in the form of a convergent series consisting of the products of Bessel and trigonometric functions, but is too cumbersome and inconvenient for use.
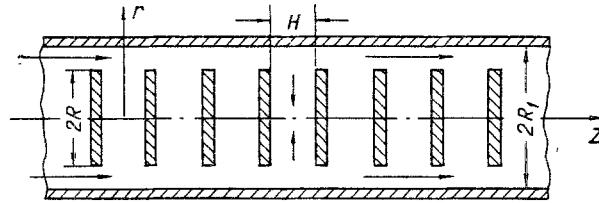
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Fig. 1. Diagram of the apparatus for depositing thin film from the vapor–gas phase.

In [1, 2], the concentration of the active component around the plates over the length of the reactor is taken to be constant, but the conditions under which this is satisfied to an extent which may be specified in advance were not elucidated. Thus, the problem was solved for any pair of plates, the conditions for the achievement of radial uniformity of the deposited-layer thickness were investigated, but the problem of achieving longitudinal uniformity (from plate to plate) was not discussed.

The aim of the present work is to model the deposition of thin films occurring in the region of reaction kinetics, which offers the possibility of estimating the influence of geometric and process parameters on the radial and longitudinal uniformity of the films.

To obtain an analytical solution of the problem, it is assumed that the concentration of active component around any pair of plates is constant, but changes in stepwise fashion from vapor to vapor; that the reaction at the plate surface is of first order, i.e., $\alpha = 1$; and that the axial component of the diffusion (along the z axis) may be neglected. The latter assumption is discussed below. In these conditions, the material balance of the diffusing material for an elementary annular volume of gas in the space between the plates for any vapor takes the form

$$2\pi r H D \; \frac{dC_i}{dr} - D \left( \frac{dC_i}{dr} - \frac{d^2C_i}{dr^2} \, dr \right) 2\pi \, (r - dr) \, H = K C_i 4 \pi r dr. \tag{2}$$

It follows from Eq. (2) that

$$\frac{d^2C_i}{dr^2} + \frac{1}{r} \, \frac{dC_i}{dr} - \frac{2K}{DH} \, C_i = 0. \tag{3}$$

Setting $y = r\sqrt{2K/DH}$ gives

$$\frac{d^2C_i}{dy^2} + \frac{1}{y} \, \frac{dC_i}{dy} - C_i = 0. \tag{4}$$

This expression is a modified zero-order Bessel equation. Its solution is [3]

$$C_i(r) = A I_0(y) + B K_0(y). \tag{5}$$

It follows from the boundary condition in Eq. (b) that $B = 0$, since $K_1(0) = \infty$. The constant of integration A is found from the boundary condition in Eq. (a)

$$C_{i,0} = A I_0 \left( R \sqrt{\frac{2K}{DH}} \right). \tag{6}$$

Then

$$C_i(r) = C_{i,0} I_0 \left( r \sqrt{\frac{2K}{DH}} \right) \Big/ I_0 \left( R \sqrt{\frac{2K}{DH}} \right). \tag{7}$$

The nonuniformity in thickness of the film deposited on the plate is usually determined by the expression [1]

$$\eta = \frac{\delta_{max} - \delta_{min}}{\delta_{max} + \delta_{min}} \tag{8}$$

and, with the given substitution, it follows from Eqs. (7) and (8) that

$$\eta(r) = \frac{I_0(r \sqrt{2K/DH}) - 1}{I_0(R \sqrt{2K/DH}) + 1} \, . \tag{9}$$

Since the modified Bessel functions are tabulated with a very small step within limits of the argument [4], the dependence obtained is very convenient for analysis and cal-
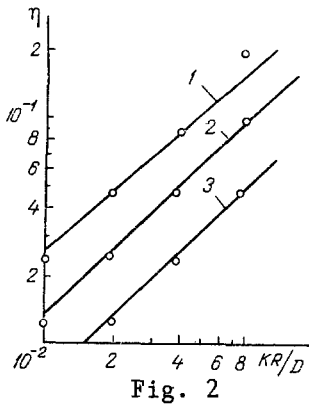
Fig. 2



Fig. 3

Fig. 2. Dependence of the radial nonuniformity on KR/D. The curves are obtained by numerical solution of Eq. (1) [1]; the points are determined from Eq. (9): 1) H/R = 0.1; 2) 0.2; 3) 0.4.
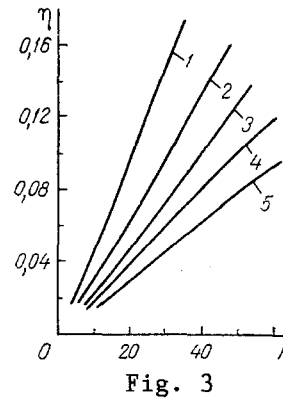
Fig. 3. Dependence of the maximum longitudinal nonuniformity on the diffusional-furnace load: 1) M/N = 100; 2) 150; 3) 200; 4) 250; 5) 300.

culation. At the same time, as shown below, the accuracy of Eq. (9) is no worse than that of the numerical solution [1] when the process is conducted in vacuo, which corresponds to the modern trend [5].

On the basis of physicochemical concepts regarding the process, the films will have sufficient uniformity over the radius if $C_i(r) \approx C_{i,0}$.

At the same time, it follows from Eq. (9) that $\eta(r) \to 0$ if $I_0(r\sqrt{2K/DH}) \to 1$. Both conditions are satisfied when $0 < y \ll 1$, since in this case [3]

$$I_0(y) \approx \frac{1}{\Gamma(0+1)} = 1. \tag{10}$$

The inequality $0 < r\sqrt{2K/DH} \ll 1$ may be satisfied by reducing R and K (reducing the temperature) or increasing H and D. These changes in R, H, and K are unfavorable, since they lead to decrease in productivity of the reactor, but increase in the diffusion coefficient is entirely possible with decrease in overall pressure of the gas mixture.

Using Eq. (9), the working pressure at which the necessary uniformity may be obtained may be determined for each specific case. For example, in the case of $Si_3N_4$ deposition by the reaction $3SiH_4 + 4NH_3 \to Si_3N_4 + 12H_2$ at 1223°K (K = 0.059 m/sec; $D_0 = 1.4 \cdot 10^{-4}$ m²/sec [1]), plate diameter 2R = 60 mm, and distance between plates 6 mm, it is necessary to have D = 0.104 m²/sec in order to obtain $\eta$ = 0.025. It follows from the dependence $D = D_0 P_0/P$ [6] that the process must be conducted at a pressure P = 134.6 Pa. In the same conditions, numerical solution gives P = 160 Pa [1].

It is evident from Fig. 2 that the approximation used here and Eq. (9) are true for small KR/D ≤ 0.1 and H/R ≤ 0.4. These constraints correspond to the inequality Da ≡ KH/D < 0.1, which is the condition for a predominant role of reaction kinetics, allowing diffusion along the z axis between the plates to be neglected (as expected in vacuum conditions).

With the above assumptions, the amount of material deposited on an elementary area of the plate is

$$dG = KC_{i,0} \frac{I_0(r\sqrt{2K/DH})}{I_0(R\sqrt{2K/DH})} 2\pi r dr, \tag{11}$$

and at each pair of plates

$$G_i = \frac{4\pi KC_{i,0}}{I_0(R\sqrt{2K/DH})} \int_0^R r I_0(r\sqrt{2K/DH}) \, dr. \tag{12}$$

The reduction in concentration of the active component in the gas mixture on account of deposition on the surface of each pair of plates follows from the material balance

$$M(C_{i,0} - C_{i+1,0}) \approx NC_{i,0}, \tag{13}$$

where the coefficients M and N are

$$M = \pi (R_1^2 - R^2) W,$$ (14)

$$N = \frac{4\pi KR I_1 (R \sqrt{2K/DH})}{I_0 (R \sqrt{2K/DH})} \sqrt{DH/2K}.$$ (15)

If Eq. (13) is used successively for each pair of plates, for the plates over the path of the gas it is found that

$$C_{n,0} = \frac{(M - N)^{n-1}}{M^{n-1}} C_{1,0}.$$ (16)

It follows from Eqs. (7), (8), and (16) that for any radius

$$\eta_{max} = \frac{\left(\frac{M}{N}\right)^{n-1} - \left(\frac{M}{N} - 1\right)^{n-1}}{\left(\frac{M}{N}\right)^{n-1} + \left(\frac{M}{N} - 1\right)^{n-1}}.$$ (17)

It is evident from Eq. (17) that $\eta(z) \to 0$ when $M \gg N$. This inequality may actually be satisfied if $R_1 \gg R$ and with considerable increase in the linear velocity of the gas mixture, which is economically unfavorable. Decrease in pressure when $W = $ const leads to increase in longitudinal nonuniformity.

In practice, the flow rate (correspondingly, the linear velocity of the gas mixture) must be chosen so that it is minimal, but sufficiently high to ensure the already-specified uniformity of the deposited layers, i.e., so that

$$\eta(z)_{max} \leqslant \eta(r) \leqslant \varepsilon.$$ (18)

How the conditions of the process (W, D, K) must be changed so that, at a given load of the diffusional furnace (n, R, H), the required uniformity may be achieved is illustrated in Fig. 3.

## NOTATION

C, concentration of the active component in the gas mixture; r, radial coordinate; R, plate radius; $R_1$, reactor radius; H, distance between the plates; D, molecular diffusion coefficient; K, rate constant of heterogeneous chemical reaction; $C_{i,0}$, concentration of active component in gas mixture, from which it flows around the i-th interval into the annular space; A, B, constants of integration; $I_0$, $K_0$, $I_1$, $K_1$, Bessel functions; i, ordinal number of the interval between two adjacent plates; n, ordinal number of plate; $\Gamma$, gamma function; $\eta$, nonuniformity coefficient of the deposited-film thickness on the plate; $\delta_{max}$, $\delta_{min}$, maximum and minimum thickness of the deposited layer; $D_0$, diffusion coefficient at normal pressure; P, working pressure of gas mixture; Da, Damköhler number; G, amount of material deposited on plates in unit time; W, linear velocity of gas flow.

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