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KINETICS OF PHYSICAL AND CHEMICAL DEPOSITION OF A SUBSTANCE FROM THE GAS PHASE IN CHANNELS

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Based on the molecular-kinetic approach, the processes of physical and chemical deposition of a substance from the gas phase on the interior surface of a channel are investigated. The problem of deposition of films which are uniform in thickness is discussed.

Problems of control of the deposition of a substance from the gas phase arise in a number of fields of new chemical technology, in particular, with deposition of thin films, as well as in problems of doping of surfaces with a certain component in order to change the physicochemical properties of materials. In a number of cases, it is necessary to create a specified distribution of the film thickness along the substrate. As this takes place, the most complicated and the least studied are the internal problems of deposition when the source of the substance deposited cannot be placed into the system (for example, with deposition of a substance on the interior surface of a narrow channel). The process of deposition can be controlled only by changing the pressure of the vapor of the substance deposited in the vicinity of the channel ends and by changing the temperature distribution along the channel walls.

In the technology of manufacturing elements of microelectronics, questions arise which are related to the filling of variously shaped channels with a certain substance [1]. In a number of cases this process is realized by means of deposition of a substance from the gas phase on condition that the regime of gas flow in channels is free molecular. This problem is closely related to the problem of coverage of the interior surface of channels with a uniform substance layer. This is caused by the fact that otherwise cavities deteriorating the quality of items manufactured can appear in the filler. As is noted in [1], deposition of coatings with a specified thickness distribution (in particular, uniform coatings) is a necessary condition for carrying out certain important operations in manufacturing elements of microelectronics. Works related to the given problem are reviewed in the same paper. A major part of the studies indicated is devoted to investigating the influence of the value of the coefficient characterizing the probability of a heterogeneous reaction in chemical deposition on the uniformity of deposition (the value of the coefficient is assumed to be constant over the entire channel length, which in turn implies the condition of isothermality of the channel wall). In what follows, on the basis of the molecular-kinetic approach we investigate the possibility of uniform deposition of a substance from the gas phase on the interior surface of a channel, which is open on both sides, in the free-molecular regime of gas flow in it. The case of both physical and chemical deposition of molecules on the side surface of the channel is considered.

The distribution of the thickness of a substance layer along the channel is determined by the resultant flux of molecules deposited on the channel wall. The problem is considered in the quasistationary approximation. It is assumed that the entire interior surface of the channel has already been covered with a layer of

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solid condensate by the beginning of the process of deposition (i.e., the process of condensate formation on the substrate surface is not treated). The film thickness throughout the process is considered to be substantially smaller than the channel radius, so that a change in the probability of molecular transition from one element of the channel surface to another owing to the growth in the condensate layer can be neglected. The growth rate of the layer thickness v is defined as

$$v = \frac{dh}{dt} = n^{-1} J \, , \tag{1}$$

where J is the density of the resultant molecular flux into the condensate and n is the number of molecules per unit volume of the condensate, which is assumed to be a constant. The flux density J of the molecules deposited in the vicinity of the point x of the interior channel surface is found from the equations (we assume further that molecules both entering the channel and outgoing from the surface are distributed according to the cosine law) [2, 3]

$$J = \alpha \left[\int_0^1 (j + I)\, K_1 \,(|x - x'|)\, dx' + N(0)\, K(x) + N(1)\, K(1 - x) \right] - j \, , \tag{2}$$

$$I = (1 - \alpha) \left[\int_0^1 (j + I)\, K_1 \,(|x - x'|)\, dx' + N(0)\, K(x) + N(1)\, K(1 - x) \right] , \tag{3}$$

where x is the dimensionless coordinate directed along the channel axis ($x = X/L$) and α is the coefficient characterizing the probability that a molecule incident on the condensate surface will not be reflected elastically from it. In the case of physical deposition (regular condensation), the condensation coefficient α_c is used as the above coefficient. With chemical deposition, this coefficient characterizes the reaction efficiency in collision of a reagent molecule with the surface as a result of which the molecule-reaction product changes to a condensed phase. The coefficient is equal to the ratio of the number of reacted molecules to the number of molecules collided with the surface. In what follows, it will be denoted as α_r.

With physical deposition, the condensation coefficient is usually considered to be independent of temperature, and in a number of cases its value is assumed to be equal to unity. The functions K and K_1 in (1) and (2) characterize the probabilities of molecular transition from one surface element to another. Their values for a cylindrical channel are determined by the expressions [4, 5]

$$K(x) = \frac{l^2 x^2 + 2}{2\,(l^2 x^2 + 4)^{1/2}} - \frac{l}{2} x \, , \quad K_1(x) = -\frac{dK(x)}{dx} \, , \tag{4}$$

where $l = L/R$.

The quantities $N(0)$ and $N(1)$ represent the densities of molecular fluxes entering the channel at $x = 0$ and $x = 1$, and I is the flux density of molecules reflected elastically; the flux density of evaporating molecules is of the form

$$j = j_0 \exp \left\{ -\frac{Q}{kT} \right\} , \tag{5}$$

where the preexponential factor j_0 is assumed further to be a constant.

In a number of cases with chemical deposition, the reevaporation of molecules from the condensate formed is very insignificant and it can be neglected, whereas the coefficient α_r substantially depends on temperature. Similarly to [6], we consider that the molecules of the initial gas collide with the surface heated, resulting in a reaction which leads to the formation of a solid phase (s) and gas molecules (g):

$$AB_{\gamma}\,(\mathrm{g}) \to A\,(\mathrm{s}) + \gamma B\,(\mathrm{g})\,. \tag{6}$$

Pyrolytic deposition of Ni from $\mathrm{Ni(CO)_4}$ provides an example of such a reaction [6]:

$$\mathrm{Ni\,(CO)_4\,(g) \to Ni\,(s) + 4\,CO\,(g)}\,. \tag{7}$$

As is noted in [6], processes of similar type are described by either a reaction of first order or the expression used for representation of the Langmuir–Hinshelwood mechanism of reaction. In what follows, we will describe the process of chemical deposition by the reaction of first order. In so doing, the coefficient α_{r} on the assumption of the Maxwellian velocity-distribution function for molecules incident on the surface and in the one-step approximation (without regard for the molecule being in the intermediate state of physical adsorption) is determined as

$$\alpha_{\mathrm{r}} = (2\pi m/kT)^{1/2}\, k_0 \exp\left\{- Q_{\mathrm{r}}/kT\right\} = \alpha_{\mathrm{r}0} \exp\left\{- Q_{\mathrm{r}}/kT\right\}. \tag{8}$$

Because of the rather weak temperature dependence of the coefficient $\alpha_{\mathrm{r}0}$, we will consider it to be a constant and allow for the temperature dependence of α_{r} just in the exponential term, similarly to [5]. We also consider that the molecules of the gas-reaction product that appear in the process of reaction do not affect the process of deposition.

Equations (1) and (2) for a cylindrical channel with the exponential approximation of the functions $K(x)$ and $K_1(x)$ [4, 5] can be solved analytically [2, 3]. With physical deposition ($j \neq 0$, α_{c} = const) the requirement on the uniformity of deposition along the channel length in the symmetric case ($N_0 = N_1$) is reduced to the following condition for the distribution of the flux density of evaporating molecules along the channel:

$$j = \alpha_{\mathrm{c}} nv \left[\frac{N_0}{nv} - \frac{l}{2} - \frac{l^2}{2} x\,(1 - x)\right] - nv\,. \tag{9}$$

It follows from (9) that for uniform deposition the density of the flux of evaporating molecules must change in a certain manner along the channel; the value of j at the ends of the channel must be higher than at its center. According to (3), this can be attained for the corresponding temperature distribution along the channel wall; the wall temperature at the central part of the channel must be lower than in the vicinity of the ends [2].

In the case of chemical deposition in the cylindrical channel, solution of Eqs. (1) and (2) by means of the mentioned approximation of the functions $K(x)$ and $K_1(x)$ with the conditions v = const and $N_0 = N_1$ and neglecting molecular reevaporation from the condensate leads to the following dependence of α_{r} on the coordinate x:

$$\alpha_{\mathrm{r}} = \left[\frac{N_0}{nv} - \frac{l}{2} - \frac{l^2 x\,(1 - x)}{2}\right]^{-1}. \tag{10}$$

For uniform deposition, as is seen from (10), the value of α_{r} should be higher at the center of the channel than at its ends, which, with account for (8), is reduced to the necessity of maintaining a higher surface temperature in the central part of the channel [7].

Thus, the foregoing shows that with both physical and chemical deposition, the uniformity of coverage of the interior channel surface with the substance deposited under the conditions mentioned can be realized through changing the values of j or α_r along the channel, which in turn is attained by creating the necessary temperature distribution along the channel wall.

It should be noted that the temperature profile depends on the heating source and the properties of the material in which the channel is placed. Thus, in the case where the channel is located in a plane-parallel plate and the influence of the channel on the temperature field in the plate can be neglected, the steady-state temperature distribution caused by the absorption of electromagnetic radiation in the plate or on its surface (an opaque plate) has the form

$$T = C_1 + C_2 X + f(X) , \tag{11}$$

where X is the coordinate counted from the side of the plate, on which the radiation is incident, and directed into the plate, the function $f(X)$ depends on the character of the absorption of radiation by the plate, and the integration constants C_1 and C_2 are determined from the corresponding boundary conditions characterizing heat exchange between the plate and the environment.

For an opaque plate $f(X) = 0$, while for a plate in which the absorption of radiation may be considered to be uniform in thickness (such an assumption is often adopted in problems on the action of microwave radiation on materials [8]), $f(X) = -\frac{q_V X^2}{2\lambda}$, where q_V is the power absorbed by unit volume of the plate and λ is the thermal conductivity of the plate. For absorption according to the Bouguer law $f(X) = -\frac{q}{\lambda\chi} \exp\{-\chi X\}$; here q is the density of the radiation flux incident on the plate and χ is the absorption coefficient of the plate. We note that the dependence of the temperature distribution on the absorption coefficient gives the basic possibility of controlling the temperature profile along the channel and accordingly the thickness distribution of the deposited film by changing the incident-radiation wavelength on which the absorption coefficient depends. This can be realized through frequency-tunable sources of radiation.

Let us consider the case where the temperature distribution in the plate thickness may be represented as

$$T(x) = T(0)\,(1 + \beta x) , \tag{12}$$

where $\beta = [T(1) - T(0)]/T(0)$ and x is the dimensionless coordinate related to the plate thickness.

For rather small temperature drops along the through channel whose axis is perpendicular to the plate surfaces, we can write the expressions for the quantities j and α_r with account for (5) and (8):

$$j(x) = j(0) \exp\{sx\} , \tag{13}$$

$$\alpha_r(x) = \alpha_r(0) \exp\{s_r x\} , \tag{14}$$

where $s = Q\beta/[kT(0)]$ and $s_r = Q_r\beta/[kT(0)]$.

The case of chemical deposition in a semiclosed cylindrical channel in the free-molecular regime of gas flow and with relation (14) fulfilled was considered in [9]. Below we discuss the case of physical deposition in a cylindrical channel which is open at both ends, with the condensation coefficient equal to unity. As this takes place, for the dimensionless density of the resultant molecular flux $J' = J/j(0)$ from (1) with the exponential approximation of the functions K and K_1 and at $s^2 \neq l^2$ we have

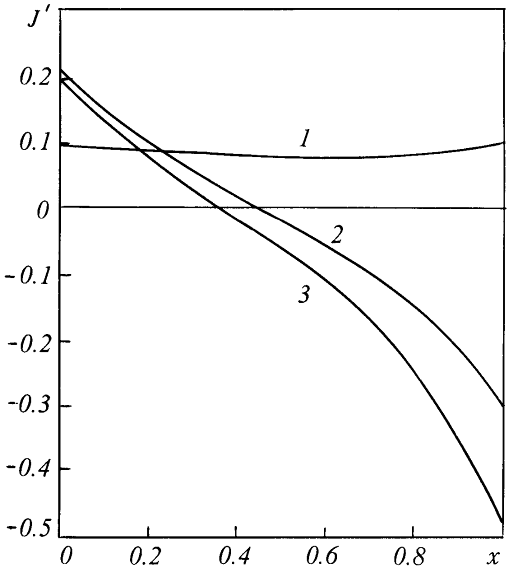

Fig. 1. Dependence of the density of the relative resultant molecular flux onto the channel wall on the dimensionless coordinate x at $N(0)/j(0) = 1.45$, $l = 3$, and the following values of the remaining parameters: 1) $N(1)/j(0) = 0.38$ and $s = -1$; 2) 0.38 and 0; 3) 0 and 0.

$$J' = \frac{1}{2}\frac{N(0)}{j(0)}\exp\{-xl\} + \frac{1}{2}\frac{N(1)}{j(0)}\exp\{-(1-x)\,l\} - \exp\{sx\} +$$

$$+\frac{l\,[\exp\{-xl\}\,(l-s) + \exp\{s - l\,(1-x)\}\,(s+l) - 2l\exp\{sx\}]}{2\,(s^2 - l^2)}. \tag{15}$$

The expression for J' provides the possibility of estimating the character of change in the resultant flux along the channel with different relationships of the quantities s, l, $N(0)/j(0)$, and $N(1)/j(0)$ for the case where there is initially a layer of the substance deposited on the channel. In particular, such an analysis enables one to answer the question whether the entire interior surface of the channel will be covered with the substance deposited in the condensation process. Figure 1 presents an example of the dependence of the quantity J' on the parameters $N(0)/j(0)$, $N(1)/j(0)$, and s for the value $l = 3$. As follows from Fig. 1, the temperature change along the channel wall may substantially improve the uniformity of deposition of the substance.

We note that for producing a film which is more uniform in thickness it is necessary that in physical deposition the temperature of the interior channel surface decrease in the direction to the cross section facing the area with a lower pressure of the substance deposited, and in chemical deposition the temperature must increase in the indicated direction.

Analysis of the process of deposition of a substance on the interior channel surface would appear to be useful both for the mentioned technology of manufacturing microelectronics elements and in realization of "healing" of microleakages that are formed in the wall separating the region of low pressure from the region with a relatively high pressure of the gas. By depositing the molecules of a certain substance which enter from the side of the region of higher pressure, on the microleakage (channel) surface one can "heat" this microleakage, having filled it with the substance deposited. As this takes place, the choice of the method of deposition (and accordingly of the substance deposited) will depend, in particular, on the temperature of the wall with a microleakage.

In conclusion, we note that knowledge of the regularities of deposition of molecules on the wall of a cylindrical channel is also necessary in investigation of the angular distribution of molecules outgoing from it [10]. The change in the temperature distribution along the interior channel surface results in a change in the spatial distribution of molecules outgoing from the channel. In the case of physical deposition where the processes of evaporation and condensation are realized on the channel surface, one can observe both the broadening and narrowing of a molecular beam depending on the sign of the temperature drop.

NOTATION

k, Boltzmann constant; T, temperature of the condensate surface; m, mass of the reactant-gas molecule; Q, evaporation heat; Q_r, activation energy of the chemical reaction; k_0, preexponential factor in the expression for the rate constant of the heterogeneous chemical reaction; L, channel length (plate thickness); R, channel radius. Subscripts: c, condensation; r, chemical reaction.

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