Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
International Journal of Heat and Mass Transfer 49 (2006) 2356–2365
International Journal of HEAT and MASS TRANSFER
www.elsevier.com/locate/ijhmt

Free-molecular gas flow in channels (pores) with physicochemical transformations on the surface

V.V. Levdansky [a,*], J. Smolik [b], P. Moravec [b]

[a] A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, 15 P. Brovka Street, Minsk 220072, Belarus
[b] Institute of Chemical Process Fundamentals AS CR, Rozvojova 135, 165 02 Prague 6, Czech Republic

Received 22 February 2005
Available online 3 February 2006

Abstract

The problems of free-molecular flow of a gas in channels are considered. The literature on the problem is reviewed. The possibility of uniform deposition of a substance on the inside surface of a cylindrical channel is analysed for the case of physicochemical transformations on this surface. The questions of spatial distribution of the molecules outgoing from the channel are discussed.
© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

A free-molecular regime of gas flow in channels is realised in the cases where the mean free path of molecules considerably exceeds the characteristic dimension of the channel (for example, its radius when the channel is cylindrical) and the influence of intermolecular collisions on the gas flow can be neglected. The gas flow in a cylindrical channel is assumed to be free-molecular, when the Knudsen number defined as the ratio of the mean free path to the channel radius is considerably higher than unity. Here, the transfer processes in the channel depend on the character of interaction of gas molecules with the channel walls. The problems of free-molecular gas flow in channels are abundant in the modern technology. This applies to a vast field of vacuum engineering, in which calculation of the conductance of different kinds of pipelines at very low pressures is a chief problem [1,2]. Such problems border also on those connected with calculation of vapour escape in sublimation drying which is usually carried out at sufficiently low vapour pressures [3]. The problems of vacuum deposition of thin films are also associated with calculation of molecular fluxes in a free-molecular flow regime [4].

The progress recently achieved in the area of microelectromechanical systems (MEMS) and nanotechnology has initiated new investigations in the field of gas flows in nanosized channels (pores) [5–7]. Interestingly that under certain conditions the nanosized objects themselves can contain nanopores. Thus, for example, the titanium nanoparticles obtained by chemical deposition can, under certain conditions of their production, be characterised by sufficiently large porosity with a pore size of 1–2 nm [8]. The gas flow in such pores can be considered free-molecular even at a high enough pressure.

We will dwell on some aspects, essential to free-molecular gas flow in channels (pores). For simplicity, further we restrict ourselves to the case where surface diffusion of molecules can be neglected. We note that the problems of free-molecular gas flow in channels may, by convention, be divided into several groups. The problems aimed at calculating the conductance of channels can be referred to the first group. Here, it suffices to determine only the resulting flux of particles emerging from the channel. For example, in the simplest case of an infinitely long cylindrical channel, its conductance is characterised by the Knudsen diffusivity which, in the case of diffuse scattering of molecules by a wall, is determined as $D_K = 2Rv/3$, where v is the thermal velocity of molecules. To calculate the conductance of the channels of finite length with impermeable surfaces, it is

* Corresponding author. Tel.: +37517 284 2250; fax: +37517 232 2513.
E-mail address: vlev5@yahoo.com (V.V. Levdansky).

0017-9310/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2005.12.001

Nomenclature

D_K	Knudsen diffusivity
h	deposited layer thickness
j	density of a flux of evaporating molecules
k	Boltzmann constant
L	channel length
l	L/R
Q	evaporation energy
Q_d	desorption energy
Q_r	activation energy of heterogeneous chemical reaction
R	channel radius
R_g	gas constant
N	density of a flux of molecules incident on the surface
T	temperature
X	coordinate directed along the channel axis
x	dimensionless coordinate ($x = X/L$)

Greek symbols

α_c	condensation coefficient
α_r	coefficient characterising the probability of heterogeneous chemical reaction
β	sticking coefficient of reactant molecules

Subscripts

c	condensation
d	desorption
g	gas
r	reaction

necessary to solve the integral Clausing equation [9]. The second group includes the problems, which require determination of the spatial distribution of the molecules escaping from the channel (in particular, the problems of vacuum deposition of films from a gas phase). The third group is comprised of the problems in which it is necessary to calculate the resulting flux of molecules onto the lateral surface of the channel. In particular, this group involves the problems of deposition of coatings (thin films) onto the inside surface of a channel. We note that the spatial distribution of the molecules outgoing from the channel depends on phase transformations or chemical reactions proceeding on the channel walls.

After the classical studies carried out by Knudsen, Clausing, and Smoluchowski a great number of works were devoted to the problems of channel conductance. These works were concerned with both derivation of approximate analytical expressions for conductance and numerical methods of analysis of the problem (a numerical solution of the integral equations that describe the process or a method of direct statistical simulation). The classical work of Clausing [9] (English translation of the article published in German in 1932) presents derivation of the integral equation that describes a free-molecular flow in a cylindrical channel. That work also considered the question on the probability of the passage of molecules through a channel in the limiting cases of rather long and short channels. In [10–12] the problem on the probability of the passage of a gas particle through a cylindrical channel is considered by means of numerical solution of the Clausing integral equation. In [13] the conductance of both cylindrical and conical channels is considered on the basis of the Monte-Carlo method. In [14] the same method was applied to determine the conductance of a capillary with an evaporating meniscus, the latter being convex, flat or concave. It was shown that the conductance of a capillary with a flat and a concave meniscuses is the same because the advantage in the area of the evaporating surface in the second case is compensated for by a higher probability for the molecules to hit this surface with their subsequent condensation. At rather high values of the capillary length-to-radius ratio, the conductance for all three cases of meniscus shape actually coincide. In [15], an analogous problem is solved by the Monte-Carlo method but with allowance for the possibility of intermolecular collisions. This method was also used in [16,17] in solving the problems of free-molecular flow of a gas in cylindrical channels. In [18,19], numerical method was applied to investigate the free-molecular flow of a gas in a channel in the presence of a heterogeneous chemical reaction on its walls.

We can single out a group of works in which the conductance of channels is determined by approximate analytical methods. We should begin a review of these from [20], in which the problem on radiation transfer in cylindrical channels was solved. However, provided the well-known analogy between the process of energy transfer by radiation and free-molecular gas flow is taken into account, this approach is also of current interest for the considered problems of the kinetic theory of gases. In [20], exponential approximation of the kernel of an integral equation analogous to the Clausing equation was used. Subsequently, the method was developed in [21,22]. In [23,24] a variation method was used to estimate the conductance in free-molecular gas flow in channels. In [25], the asymptotic behaviour of a resulting flux of particles for long tubes was investigated by the Wiener–Hopf method. An additional information on the problems of the conductance of channels in both free-molecular and intermediate regimes of gas flow can be found in [26].

The problem of spatial distribution of molecules emerging from channels is also related to solving the Clausing equation because the knowledge of the flux density of molecules outgoing from the channel walls is necessary to determine this distribution [21]. The problem of angular

distribution of molecules for cylindrical channels with diffusely scattering walls was considered in [21,27–29]. In this case, deviation of angular distribution from the cosine law depends on the ratio between the length of a channel and its radius (geometrical factor). Of more interest, and more adaptable as concerns the control, is the case where different physicochemical transformations are realised on the channel walls [19,30,31]. In [19], an angular distribution of a molecular beam at the exit from a cylindrical channel in the presence of a heterogeneous chemical reaction on the channel wall resulting in disappearance of the particles, as such, is investigated. In [30], an angular distribution of molecules in the case of escape, from the Knudsen chamber, of a dissociating gas containing atoms and diatomic molecules was found. The problem of spatial distribution of atomic beams with allowance for the recombination of atoms on the wall of a cylindrical channel was investigated in [31]. A spatial distribution of molecules can be used to calculate the distribution of the flux density of molecules incident on the substrate placed opposite the exit of the channel (particle detector) [32,33]. However, this calculation is correct only for sufficiently large values of the ratio between the distance to the substrate and the channel radius. In the general case, the distribution of the flux density of particles incident on the substrate can be found by direct calculation of the flux of molecules (without invoking the spatial distribution). Such an approach was developed in [34,35].

It should be noted that both mass transfer in the channel on the walls of which the processes of evaporation–condensation or heterogeneous chemical reaction are realised and the angular distribution of outgoing molecules depend on temperature distribution along the channel. This can be used to control molecular fluxes both in the channel and outside it (the latter fact is important for forming the required angular distribution of molecules outgoing from the channel as well as obtaining coatings with a certain distribution of thickness over the substrate located normally to the channel axis). Below, we investigate the influence of the temperature drop along the length of a cylindrical channel with an evaporating lateral surface on the resulting flux of molecules both those escaping from the channel and falling on this surface as well as on the angular distribution of the molecules emerging from the channel. To find the above-mentioned quantities, it is necessary to know the distribution of the flux density of the molecules outgoing from the channel surface.

2. Free-molecular gas flow in a nonisothermal channel with consideration for phase transformations on its inside surface

A free-molecular gas flow in a cylindrical nonisothermal channel, when phase transition and/or heterogeneous chemical reaction was realised on its lateral surface and/or bottom was investigated in [36–54]. We note that the nonuniformity of phase transition along the channel length can be due not only to nonisothermicity but also to other factors. For example, the lateral surface of the channel which is initially covered with a condensed phase at a vapour pressure near its exit end less than the saturated vapour pressure will be cleaned with time of condensate layer. The given situation occurs in the problems of sublimation drying. The opposite case is realised when a part of the lateral surface of the channel is covered with a film of condensed phase on deposition of a substance from a gas phase. One of the reasons for a change in the evaporation intensity along the channel (capillary) length can be the difference in the energy of the evaporation. For example, in [55] it is shown that under certain conditions the thickness of a polar liquid film covering the capillary surface can undergo a discontinuous change, which leads to a change in the evaporation energy. The nonisothermicity of the channel walls may result in a situation where a part of the channel surface is covered with a condensate layer and the other part is free of it. Moreover, relationship between the covered and uncovered parts, which in turn determines both the channel conductance and the angular distribution of the molecules outgoing from the channel, depends on the temperature drop along the channel [45].

For the density of a flux of the molecules escaping from the lateral surface of a cylindrical channel (I^+), neglecting a change in the channel geometry due to substance evaporation or deposition on the channel walls fully covered with condensate, we can write the following equation [36]:

$$I^+ = j + (1-\alpha_c) \times \left[\int_0^1 I^+ K_1(|x-x'|)\,dx' + N(0)K(x) + N(1)K(1-x)\right], \quad (1)$$

where x is the dimensionless coordinate directed along the channel axis ($x = X/L$); $N(0)$ and $N(1)$ are the densities of the fluxes of molecules entering into the channel at $x = 0$ and $x = 1$, and α_c is the condensation coefficient (which further is assumed to be equal to the evaporation coefficient); usually in physical deposition α_c is considered to be temperature-independent. The functions K and K_1 in Eq. (1) characterise the probabilities of the transition of molecules from one surface element to another (in what follows the spatial distribution of molecules both entering into the channel and escaping from its surface will be considered corresponding to the cosine law). Their values for the cylindrical channel are determined as [9,36]

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

The temperature dependence of the flux density of evaporating molecules j can be represented in the form [36]

$$j = \alpha_c A \exp\left\{-\frac{Q}{R_g T}\right\} = B \exp\left\{-\frac{Q}{R_g T}\right\}, \quad (3)$$

where factors A and B are assumed to be constants because of their weak dependence on the temperature.

We consider the case where a temperature change along the channel looks like

$$T = T_0\left(1 + \frac{T_1 - T_0}{T_0}x\right) = T_0(1 + \varepsilon x), \tag{4}$$

where T_0 and T_1 are the temperatures of the channel walls at $x = 0$ and $x = 1$, respectively, and $\varepsilon = (T_1 - T_0)/T_0$. When $|\varepsilon| \ll 1$, Eq. (3) can be written as

$$j = j_0 \exp\left\{\frac{\varepsilon Q}{R_g T_0}x\right\} = j_0 \exp\{sx\}, \tag{5}$$

where $s = \varepsilon Q/(R_g T_0)$ and j_0 is the value of j at $x = 0$.

When the function $K(x)$ is approximated by exponential function [20–22]

$$K(x) = \frac{1}{2}\exp\{-xl\} \tag{6}$$

and with allowance for the relationship between the functions K_1 and K Eq. (1) can be solved analytically.

We consider the free-molecular flow in a channel with phase transformations on its lateral surface. Double differentiation of Eq. (1), subject to Eqs. (5) and (6), and the subsequent combination of the resulting equation with the initial one allow us to pass from the integral equation to a differential one whose solution for $s^2 \neq \alpha_c l^2$ has the form [36,39]

$$I^+ = a_1 \exp\{cx\} + a_2 \exp\{-cx\} + \frac{b}{s^2 - \alpha_c l^2}\exp\{sx\}, \tag{7}$$

where $b = j_0(s^2 - l^2)$. Solution of Eq. (1) for $s^2 = \alpha_c l^2$ is

$$I^+ = a_1' \exp\{cx\} + a_2' \exp\{-cx\} + \frac{b}{2s}x\exp\{sx\}. \tag{8}$$

The constants a_1, a_2, a_1', and a_2' are determined on substitution of the corresponding solutions into the initial integral equation.

The analytical expression obtained for I^+ makes it possible to analyse a number of the problems related to calculation of the resulting flux of molecules both escaping from the channel and condensing on its lateral surface. In addition, a knowledge of the value of I^+ allows one to find the angular distribution of the molecules outgoing from the channel.

3. The resulting flux of the molecules outgoing from a channel with evaporating walls

For a number of problems of chemical technology (in particular, in drying processes), calculation of the resulting flux of the molecules outgoing from a capillary-porous body is a highly urgent problem. We consider this problem on a model of a single cylindrical capillary in which a free-molecular regime of vapour flow is realised. For the density of a flux of the molecules escaping from the cylindrical channel (capillary) with evaporating lateral and bottom surfaces under the condition of vacuum near the exit section ($N(1) = 0$), the following expression can be written [39]:

$$N' = I_0^+ K_2(1) + 2l\int_0^1 I^+ K(1 - x)\,dx. \tag{9}$$

Here, $K_2(x)$ is related to $K(x)$ as

$$\frac{dK_2}{dx} = -2lK \tag{10}$$

and the density of the flux of molecules outgoing from the evaporating bottom (I_0^+) that is supposed to be flat has the form (in what follows, the radial distribution of the molecules escaping from the bottom is neglected):

$$I_0^+ = j_0 + 2l(1 - \alpha_c)\int_0^1 I^+(x)K(x)\,dx, \tag{11}$$

where j_0 is the density of a flux of the molecules evaporating from the bottom.

Substitution of the solution for I^+ (which can be obtained by the above-described method) allows us to find the value of N'. Thus, e.g., when $\alpha_c = 1$ and $s^2 \neq l^2$, for evaporation into vacuum ($N(1) = 0$), Eqs. (5), (9), and (11) yield

$$N' = j_0 \exp\{-l\}\left[1 + \frac{l}{s + l}(\exp\{s + l\} - 1)\right]. \tag{12}$$

4. Uniform deposition of a substance on the inside surface of a cylindrical channel

The problems of controlling substance deposition from a gas phase emerge in a number of fields of new chemical technology, in particular, in deposition of thin films as well as in the problems of surface doping by a definite component to change the physicochemical properties of materials. In some cases (for example, in the technology of production of microelectronics elements), it is necessary to implement the prescribed distribution of film thickness over a substrate. Here, the internal problems of the deposition, when a source of the deposited substance cannot be placed inside the system (e.g., in substance deposition on the lateral surface of a narrow channel), are the most complex and least studied ones. Here, the process of deposition can be controlled only by changing the pressure of the deposited substance vapours near the channel ends and the temperature distribution along the channel wall. Substance deposition on the walls of the channel can lead to blocking of the latter resulting in the deterioration of the progress of a technological process (for example, in the processes of substance separation on gas filtration in porous bodies as well as in drying processes). On the other hand, in the technology of production of microelectronics workpieces, the questions arise which are related to filling channels of different shapes with a definite substance [56]. In a number of cases, the process of filling is realised by substance deposition from a gas phase under the condition of a free-molecular gas flow regime in channels. It should be noted that in nonisothermal case, the channels (pores) will be "overgrown" more intensively near the ends that

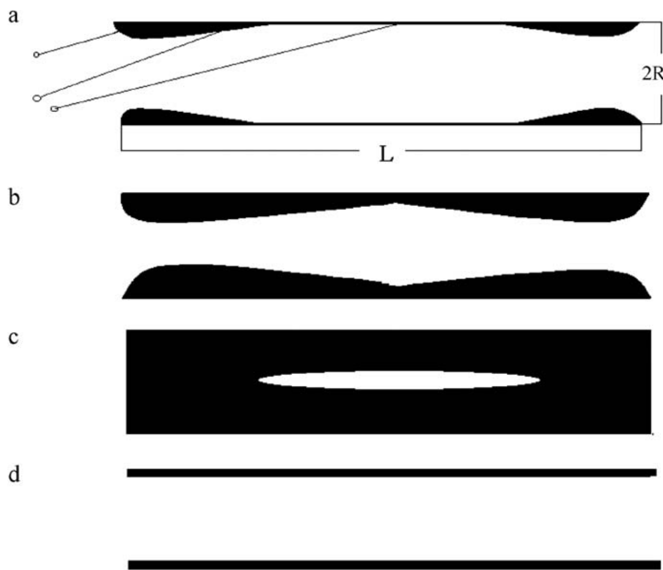


Fig. 1. Geometrical scheme of substance deposition in a cylindrical channel (symmetrical case) for deposition stages in an isothermal channel with cavity formation (a–c) and uniform deposition (d).

extend into a gas phase, in which deposited particles are present. This can lead to complete blockage of the channel with formation of a cavity inside channel (Fig. 1). This problem is directly related to the problem of coating the inside surface of channels with a uniform layer of substance. This is due to the fact that otherwise cavities can appear in the filler and this deteriorates the quality of the articles produced. As noted in [56], deposition of coatings with a set distribution of the thickness (in particular, deposition of uniform coatings) is a necessary condition to carry out some important manipulations in production of microelectronics elements.

The problems of chemical deposition from a gas phase in half-closed channels were considered in [56–58]. It was shown, in particular, that uniformity of the deposited layer thickness increases on decrease in the coefficient α_r which characterises the probability of a heterogeneous chemical reaction on collision of a reactant molecule with a wall (a change in α_r along the channel was not considered in the works mentioned, which corresponded to the isothermicity of the channel wall). In [59], the problem of chemical deposition was investigated for a half-closed channel with realisation of a linear temperature distribution along the channel wall. It was shown that a temperature change along the channel wall can result in both more uniform deposition of a substance on the walls and optimisation of filling the channel with a certain substance.

Below we consider the problem of uniform deposition of substance from a gas phase on the lateral surface of a cylindrical channel, open at both ends, with a free-molecular regime of a gas flow in it [50–54]. The cases of both physical and chemical deposition of molecules on the lateral surface of the channel are analysed.

The problem is considered in a quasi-stationary approximation. It is supposed that before the beginning of the process of deposition the entire lateral surface of the channel has already been covered with a layer of a solid condensate (i.e., the process of formation of a solid film on the substrate surface is not considered). The film thickness is taken to be substantially less than the channel radius throughout the entire process, so that the change in the probability of the transition of molecules from one element of the surface to another due to the growth of the condensate layer can be neglected. The rate of the growth of the layer thickness v is defined as

$$v = \frac{\mathrm{d}h}{\mathrm{d}t} = n^{-1}J, \tag{13}$$

where J is the density of the resulting flux of molecules into the condensate and n is the number of molecules in a unit volume of the condensate supposed to be constant.

The density J of the flux of the molecules deposited in the vicinity of a point x of the lateral surface of the channel is found from the equations [53]

$$J = \alpha\left[\int_0^1 (j+I)K_1(|x-x'|)\,\mathrm{d}x' + N(0)K(x) + N(1)K(1-x)\right] - j, \tag{14}$$

$$I = (1-\alpha)\left[\int_0^1 (j+I)K_1(|x-x'|)\,\mathrm{d}x' + N(0)K(x) + N(1)K(1-x)\right], \tag{15}$$

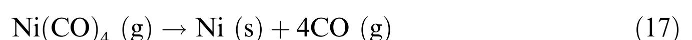
where I is the density of the flux of molecules elastically reflected from the surface of the condensed phase.

In physical deposition, α is the condensation coefficient α_c (frequently, the value of α_c is assumed equal to unity). In chemical deposition, if a heterogeneous chemical reaction is described by a one-stage scheme, the coefficient $\alpha = \alpha_r$ characterises the probability of a reaction on collision of a reagent molecule with the surface, as a result of which a molecule-product of the reaction passes into the condensed phase. This coefficient is equal to the ratio of the number of reacted molecules to the number of the molecules that collided with the surface. The evaporation of molecules from the condensate formed on chemical deposition in a number of cases is insignificant and can be neglected.

By analogy with [60] we consider that the molecules of the initial gas-reactant collide with a heated surface, and this is accompanied by a reaction that leads to formation of a solid phase (s) and gas molecules (g):

$$AB_\gamma\ (g) \rightarrow A\ (s) + \gamma B\ (g). \tag{16}$$

As an example of such a reaction we can refer to pyrolytic deposition of Ni in decomposition of $Ni(CO)_4$ [60]



$$Ni(CO)_4\ (g) \rightarrow Ni\ (s) + 4CO\ (g) \tag{17}$$

The temperature dependence of the coefficient α_r in the one-stage approximation (without regard for the residence of a molecule in the intermediate state of physical adsorption) for the first order reaction can be represented as

$$\alpha_r = \alpha_r' \exp\{-Q_r/(R_g T)\}, \quad (18)$$

where Q_r is the energy of a chemical reaction and the pre-exponential factor is supposed to be constant.

At sufficiently low temperature drops along the channel and allowance for (4), for the quantity α_r we can write the expression which is analogous to Eq. (5):

$$\alpha_r(x) = \alpha_r(0) \exp\{s_r x\}, \quad (19)$$

where $s_r = Q_r \varepsilon/(R_g T_0)$ and $\alpha_r(0)$ is the value of α_r at $x = 0$.

We consider that the molecules which appear as a result of the reaction do not influence the deposition process. Using the exponential approximation of the functions K and K_1, from Eqs. (14) and (15) it is possible to find the conditions necessary for uniform deposition of a substance on the lateral surface of the channel.

In physical deposition ($j \neq 0$, $\alpha_c = \text{const}$), the requirement of the uniformity of deposition along the channel length in the symmetrical case ($N(0) = N(1) = N$) is reduced to the following condition of distribution of the flux density of evaporating molecules along the channel [53]:

$$j = \alpha_c C \left[\frac{N}{C} - \frac{l}{2} - \frac{l^2}{2} x(1-x)\right] - C, \quad (20)$$

where $C = nv = J = \text{const}$ is the value of the resulting flux of molecules into the condensate which is constant along the channel. It follows from (20) that for uniform deposition the flux density of evaporating molecules should change in a certain way along the channel, with the value of j at the channel ends being larger than at the centre.

In chemical deposition in a cylindrical channel, the solution of Eqs. (14) and (15) by means of the above-mentioned exponential approximation of $K(x)$ and $K_1(x)$, neglecting the reevaporation of molecules from the condensate under the symmetrical conditions (when the flux densities of reactant molecules N_r are the same at both ends of the channel), the condition of uniform deposition results in the following dependence of α_r on the coordinate x [53]:

$$\alpha_r = \left[\frac{N_r}{C} - \frac{l}{2} - \frac{l^2 x(1-x)}{2}\right]^{-1}. \quad (21)$$

It is seen from Eq. (21) that for uniform deposition the value of α_r must be higher at the channel centre than at the ends, which, with allowance for Eq. (18), reduces to the need for the maintenance of higher temperature of the surface at the central part of the channel.

Thus, the foregoing shows that in both physical and chemical deposition, the uniformity of coating the inside surface of the channel with deposited substance under the specified conditions may be realised by a changing the value of j or α_r along the channel, which in turn is achieved by creating the necessary temperature distribution along the channel wall. With allowance for Eqs. (3), (14), (15) and (18), for the temperature distribution needed to obtain uniform coating along the channel length in physical and chemical deposition under the symmetrical conditions for the flux densities of the molecules entering the channel through its ends, we can obtain the following expressions [50–52]:

$$T = \frac{Q}{R_g \ln\left\{\frac{\alpha_c C[N/C - l/2 - l^2 x(1-x)/2] - C}{B}\right\}^{-1}}, \quad (22)$$

$$T = \frac{Q_r}{R_g \ln\{\alpha_r'[N_r/C - l/2 - l^2 x(1-x)/2]\}}. \quad (23)$$

It is seen from Eqs. (22) and (23) that a value of T decreases with Q and Q_r. We note that in uniform deposition the assumption of small layer thickness can be eliminated in principle because the geometry of the channel does not change (only its radius undergoes a change). The law of a change with time in the radius R_s of the channel formed by the deposited layer of a solid substance has the form

$$R_s = R_{s0} - h(t), \quad (24)$$

where $h(t)$ is the thickness of the condensate layer that changes with time and R_{s0} is the initial radius of the channel the walls of which represent the condensate layer.

It follows from Eqs. (22)–(24) that, in the general case, to attain uniform deposition at large enough thickness of the deposited layer the temperature should change according to a certain law, not only with coordinate but also with time. Here, in physical deposition the temperature at the channel ends must be higher than at its centre, whereas in chemical deposition quite the reverse is true. Eqs. (23) and (24) also yield limitations on the maximum rate of substance deposition which depends on the ratio of the length of the channel to its radius. The higher this value, the less can be the rate of deposition.

In [50], the case of physical deposition is considered, where the quantity J is the function of the coordinate (i.e., substance deposition along the channel follows a certain law).

Earlier, the one-stage scheme was used to describe a heterogeneous chemical reaction (without regard for the residence of a reactant molecule in an intermediate adsorbed state). In a two-stage scheme of a heterogeneous chemical reaction, the process of adsorption of reactant molecules on the phase transition surface is taken into account. Here, with small surface coverage by adsorbed molecules, the following equation can be obtained for temperature distribution along the channel wall that is required for uniform substance deposition with neglect of reevaporation of molecules deposited [54]

$$T(x) = \frac{Q_r - Q_d}{R_g \ln\left\{\frac{k_{r0}}{k_{d0}}\left[\beta\left(\frac{N_r}{C} - \frac{l}{2} - \frac{l^2 x(1-x)}{2}\right) - 1\right]\right\}}. \quad (25)$$

where k_{d0} and k_{r0} are the pre-exponential factors for the constants of the rates of desorption and chemical reaction which are supposed to be constant and β is the sticking coefficient of reactant molecules.

Fig. 2 shows the distributions of the dimensionless temperature $T'(x) = T(x)/(|Q_r - Q_d|/R_g)$ along the channel

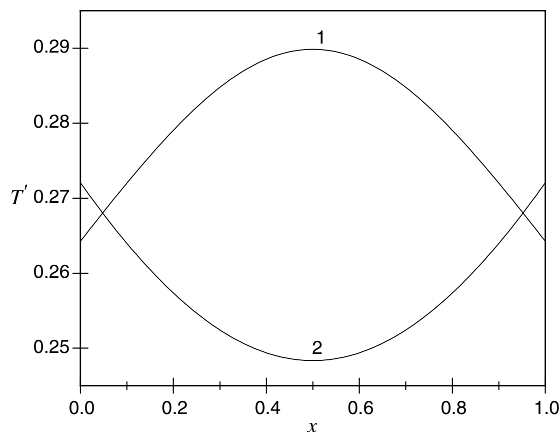


Fig. 2. Distribution of dimensionless temperature T' necessary for uniform chemical deposition in a cylindrical channel at $l = 10$, $N_r/C = 50$ and different values of other parameters: 1—$Q_r > Q_d$, $k_{d0}/k_{r0} = 1$, $\beta = 1$; 2—$Q_r < Q_d$, $k_{d0}/k_{r0} = 600$, $\beta = 0.36$.

which lead to uniform chemical deposition for the cases of $Q_r < Q_d$ and $Q_r > Q_d$. In the former case the values of parameters k_{d0}/k_{r0} and β used in [61] are taken: $k_{d0}/k_{r0} = 600$ and $\beta = 0.36$ (in [61], the value of $Q_d - Q_r$ was assumed to be equal to 3.8 kcal/mol). For $Q_r > Q_d$, the values $k_{d0}/k_{r0} = 1$ and $\beta = 1$ are taken. It is seen from Fig. 2 that in this case the function $T'(x)$ has a maximum at the channel centre and for $Q_r < Q_d$ it is characterised by a minimum.

The foregoing shows that the temperature distribution that is necessary for uniform chemical deposition of a substance in a channel depends substantially on relationship between the energy of activation of a heterogeneous chemical reaction and the energy of desorption of nonreacted reactant molecules, and it can be characterised by both maximum and minimum at different relationships between Q_r and Q_d. However, in the one-stage approach (without regard for molecule residence in the intermediate state of physical adsorption), the temperature distribution leading to uniform chemical deposition along the channel is characterised only by a maximum [52].

It should be noted that the temperature profile along the wall of a thin channel disposed in a plate depends on the source of heating and the properties of the material in which the channel is located [53]. For example, during heating of the plate which is opaque relative to incident radiation, the temperature distribution in it is linear. But when radiation absorption can be considered uniform over the plate volume, the maximum temperature is reached at the plate centre (such a situation can take place during action of microwave radiation). In the general case, the temperature distribution depends on the absorption coefficient. This, in principle, allows one to control the temperature profile along the channel and, correspondingly, the distribution of thickness of a deposited film by changing the wavelength of incident radiation on which the absorption coefficient depends. Such a control, in particular, can be realised by frequency-changed radiation sources.

We note that sufficiently uniform coatings on the channel walls can be obtained also in the simplest case of a linear temperature profile. As indicated above, the case of chemical deposition in a half-closed cylindrical channel with a free-molecular regime of gas flow for a linear temperature distribution along the wall was considered in [59]. Below we discuss the case of physical deposition in a cylindrical channel open at both ends with the condensation coefficient equal to unity and linear temperature distribution along the channel. Here, for the dimensionless density of the resulting flux of molecules onto the channel wall $J' = J/j_0$ with the exponential approximation of functions K and K_1 and $s^2 \neq l^2$ we obtain

$$J' = \frac{1}{2}\frac{N(0)}{j_0}\exp\{-xl\} + \frac{1}{2}\frac{N(1)}{j_0}\exp\{-(1-x)l\} - \exp\{sx\} + \frac{l[\exp\{-xl\}(l-s) + \exp\{s - l(1-x)\}(s+l) - 2l\exp\{sx\}]}{2(s^2 - l^2)}. \tag{26}$$

This expression for J' makes it possible to estimate the character of a change in the resulting flux along the channel with different relationships between the values of s, l, $N(0)/j_0$ and $N(1)/j_0$ in the case where initially there is a layer of the deposited substance on the channel surface. In particular, this analysis enables one to clarify whether the entire lateral surface of the channel will be covered with deposited substance during condensation. Fig. 3 shows an example of the dependence of J' on the parameters $N(0)/j_0$, $N(1)/j_0$ and s at $l = 3$. As follows from the figure, a temperature change along the channel wall (even in the considered simplest case of a linear temperature distribution along the channel) can substantially improve the uniformity of substance deposition.

We note that in physical deposition, to obtain a more uniform layer of substance along the channel length, it is necessary that the temperature of the lateral surface should

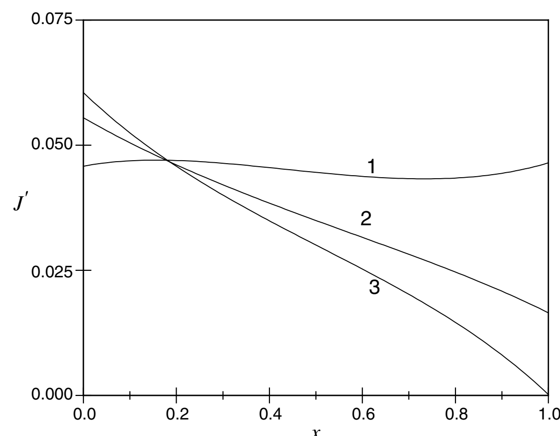


Fig. 3. Dependence of the density of the relative resulting flux of molecules onto the channel wall on the dimensionless coordinate x at $N(0)/j_0 = 1.29$, $N(1)/j_0 = 0.41$, $l = 3$ and different values of s: 1—$s = -0.75$; 2—$s = -0.65$; 3—$s = -0.6$.

decrease in the direction toward the section facing the region with a lower pressure of the deposited gas. In chemical deposition, the same purpose may be achieved if the temperature is increased in the direction toward the channel section that faces the region with a lower pressure of the gas-reactant.

An analysis of substance deposition on the lateral surface of a channel can appear to be useful both for the above-mentioned technology of production of microelectronics elements and in realisation of "healing" microleakages formed in a wall that separates the region of low pressure from that with a relatively high pressure of a gas. By depositing the molecules of a certain substance, which enter from the region of higher pressure, on the lateral surface of a microleakage (channel), it is possible to "heal" the given microleakage by filling it with the substance deposited. Here, a choice of the deposition method (and correspondingly of the substance deposited) will depend, in particular, on the temperature of the wall which contains a microleakage.

5. Angular distribution of molecules outgoing from a nonisothermal channel with evaporating inside surface and their deposition on a flat substrate

Earlier the problems of a free-molecular flow of a gas in a cylindrical channel with phase transformations or heterogeneous chemical reactions on its inner surface were considered. Also of interest is the question of spatial distribution of the particles outgoing from such a channel. This problem is of current interest in connection with the problem of control of the spatial distribution of molecular beams as well as of substance deposition from a gas phase (in particular, of vacuum deposition of thin films) [62]. In [41–49], the question of the dependence of the spatial distribution of a molecular (or atomic) beam on a temperature drop along the cylindrical channel was discussed in the case of evaporation (sublimation)–condensation processes on the lateral surface and the bottom of the channel. The ratio between the intensity of the flux of molecules leaving the channel at an angle θ to its axis and the intensity at $\theta = 0$ that characterises the spatial distribution of the molecular beam can be written as [27]

$$f(\theta) = W(\theta)\cos\theta, \tag{27}$$

where the function W is expressed as follows:

$$W(\theta) = \frac{4l}{\pi I_0^+}\int_0^{\frac{\operatorname{tg}\theta}{2}} I^+(x)(1 - l^2\xi^2)^{1/2}\,\mathrm{d}\xi + 1 - \frac{2}{\pi}\left[\arcsin u + u(1-u^2)^{1/2}\right] \quad \text{at } \theta \leqslant \operatorname{arctg}\frac{2}{l}, \tag{28}$$

$$W(\theta) = \frac{4l}{\pi I_0^+}\int_0^{\frac{1}{l}} I^+(x)(1 - l^2\xi^2)^{1/2}\,\mathrm{d}\xi \quad \text{for } \theta > \operatorname{arctg}\frac{2}{l}. \tag{29}$$

Here, as previously, $x = X/L$ is the dimensionless coordinate reckoned from the bottom assumed to be flat. The quantities ξ and u are defined as $\xi = [(1-x)\operatorname{tg}\theta]/2$ and $u = [l\operatorname{tg}\theta]/2$. The terms outside the integral correspond to the molecules straight-flying from the bottom to the channel exit without collisions with the walls.

Thus, to find the spatial distribution of the molecules outgoing from the channel, it is necessary to know the distribution of the density of the flux of particles leaving the lateral surface of the channel which is described by Eq. (1). It follows from Eqs. 1 and (27)–(29) that the spatial distribution of escaping molecules depends on the dimensionless parameters u and l and on the condensation (evaporation) coefficient α_c.

When $\alpha_c = 1$, there is no need to solve the integral equation. Here, for $s \ll 1$ Eqs. (28) and (29) yield

$$W(\theta) = 1 + \frac{2s}{\pi}\left[u(1-u^2)^{1/2} + \arcsin u + \frac{2}{3u}\{(1-u^2)^{3/2} - 1\}\right] \quad \text{at } \theta \leqslant \operatorname{arctg}\frac{2}{l}, \tag{30}$$

$$W(\theta) = 1 + s\left(1 - \frac{4}{3\pi u}\right) \quad \text{for } \theta > \operatorname{arctg}\frac{2}{l}. \tag{31}$$

It follows from Eqs. (27), (30), and (31) that at $\alpha_c = 1$ in an isothermal case ($s = 0$) we have $W(\theta) = 1$ for all angles θ, which corresponds to the fulfillment of the cosine law for the particles escaping from the channel. When $\alpha_c \neq 1$ and $s \neq 0$, the spatial distribution is found by numerical integration in Eqs. (28) and (29) with the use of the approximate analytic solution of Eq. (1) obtained by the above-mentioned method [49]. For the case where evaporation occurs only on the bottom, $W(\theta)$ is determined by the expression presented in [21].

It follows from the results of calculation of the spatial distribution of the molecular beam outgoing from the channel with an evaporating lateral surface that a change in the temperature drop along the surface can result in beams which can be both narrower as compared with the isothermal case and wider as well as the beams characterised by a maximum at a certain value of the angle θ [41,49]. Here, the influence of the temperature drop on the spatial distribution manifested more strongly for larger values of the condensation coefficient.

A knowledge of the angular distribution of the vapour molecules outgoing from the channel with an evaporating surface allows one to calculate also the process of deposition of vapour molecules on a flat substrate located perpendicularly to the channel axis provided that the distance from the channel exit section to the substrate is much larger than the channel radius. Under the specified condition, the source of molecules can be considered as a certain effective point source with the spatial distribution of molecules corresponding to that for a cylindrical channel [32]. Such a representation allows one to find the flux of molecules incident on the substrate surface element characterised by the angle θ, which in turn enables one to calculate the distribution of film thickness over the substrate. It is shown in [49]

that, in principle, the process of deposition of molecules on the substrate can be controlled by a change in the temperature distribution along the channel wall. This provides a way of obtaining both uniform enough coatings over a certain range of the radial coordinate and coatings characterised by a maximum in thickness.

The point source approximation fails if the substrate is located close enough to the channel exit. In this case, a more general method of calculation should be used when the film thickness distribution is determined not only by an angle at which particles escape from the channel but also by the coordinate of the element of lateral surface from which they escape. Based on the above-mentioned general method of calculation, an analysis of deposition of the molecules, leaving the channel with an evaporating lateral surface, on a flat substrate for arbitrary ratios between the distance from the channel exit section to the substrate and the channel radius was conducted [41,49]. It was shown that for sufficiently large values of the ratio, the given method leads to the results approaching those obtained by the above method of an equivalent point source.

Thus, by changing the temperature along the channel with an evaporating inside surface it is possible to influence the distribution of the condensate film thickness over the substrate. It should be noted that, if the evaporation of molecules from the substrate is taken into account, the rate of substance deposition is determined by a difference between the densities of the fluxes of the condensing and evaporating molecules. Here the possibility of controlling the process of substance deposition on the substrate both due to the temperature change along the channel with an evaporating surface and creation of a temperature profile on the deposition surface appears. We note that the considered method of controlling the process of vacuum deposition allows one to obtain the substance layers with different kinds of radial nonuniformity.

6. Conclusions

A review of the works on free-molecular flows in cylindrical channels with both impermeable surfaces and physicochemical transformations on the lateral surface of a channel is presented. Consideration is given to the problems of flow in nonisothermal channels with evaporating surfaces. The problems of uniform deposition of a substance on the lateral surface of a channel with both physical and chemical deposition are analysed. The possibility of controlling the spatial distribution of the molecular beam escaping from the cylindrical channel with an evaporating lateral surface is discussed. The problem of deposition of these molecules on a flat substrate placed normally to the channel axis near the exit section is also considered.

References

[1] G.L. Saksagansky, Molecular Flows in Complex Vacuum Structures, Atomizdat, Moscow, 1980.
[2] Yu.N. Lyubitov, Effusion and processes on the surface, Usp. Fiz. Nauk 119 (4) (1976) 641–688.
[3] A.V. Luikov, Drying Theory, Energiya, Moscow, 1968.
[4] C.F. Powell, J.H. Oxley, J.M. BlocherJr. (Eds.), Vapor Deposition, Wiley, New York, London, Sydney, 1968.
[5] S. Roy, R. Raju, H.F. Chuang, B.A. Cruden, M. Meyyappan, Modeling gas flow through microchannels and nanopores, J. Appl. Phys. 93 (8) (2003) 4870–4879.
[6] S. Naris, D. Valougeorgis, F. Sharipov, D. Kalempa, Discrete velocity modeling of gaseous mixture flows in MEMS, Superlattices Microstruct. 35 (3–6) (2004) 629–643.
[7] D. Cao, J. Wu, Self-diffusion of methane in single-walled carbon nanotubes at sub- and supercritical conditions, Langmuir 20 (9) (2004) 3759–3765.
[8] F. Kirkbir, H. Komiyama, Formation and growth mechanism of porous, amorphous, and fine particles prepared by chemical vapor deposition. Titania from titanium tetraisopropoxide, Canadian J. Chem. Eng. 65 (1987) 759–766.
[9] P. Clausing, The flow of highly rarefied gases through tubes of arbitrary length, J. Vacuum Sci. Technol. 8 (5) (1971) 636–646.
[10] J.C. Helmer, Solution of Clausing's integral equation for molecular flow, J. Vacuum Sci. Technol. 4 (6) (1967) 360–363.
[11] T.D. Sandry, F.D. Stevenson, Observations on radiation heat transfer and molecular conductance, J. Chem. Phys. 55 (8) (1971) 4150–4151.
[12] A.S. Berman, Free-molecule flow through a long rotating tube, J. Appl. Phys. 40 (12) (1969) 4972–4975.
[13] W.K. Talley, S. Whitaker, Monte Carlo analysis of Knudsen flow, J. Comp. Phys. 4 (3) (1969) 389–410.
[14] T.D. Sandry, F.D. Stevenson, Molecular conductance from a curved surface through a cylindrical hole by Monte Carlo methods, J. Chem. Phys. 53 (1) (1970) 151–155.
[15] P.T. Choong, E.A. Mason, Calculation of obstruction effects on rarefied particle streaming through short tubes, J. Appl. Phys. 42 (10) (1971) 3755–3761.
[16] R. Gorenflo, M.G. Pacco, B.M.U. Scherzer, Monte Carlo simulation of Knudsen gas flow with due allowance for the sojourn time, Z. Angew. Phys. 22 (6) (1967) 500–505.
[17] J.W. Ward, M.V. Fraser, Gas transfer from a large reservoir to a small tube. The initial flow problem, Z. Angew. Phys. 29 (6) (1970) 336–339.
[18] F.H. Verhoff, W. Strieder, Numerical studies of Knudsen diffusion and chemical reaction in capillaries of finite length, Chem. Eng. Sci. 26 (2) (1971) 245–253.
[19] A.I. Livshits, I.M. Metter, L.E. Rikenglaz, Angular distribution of a molecular beam at the exit of a cylindrical channel with the first-order reaction on the channel walls, Zh. Tekh. Fiz. 41 (2) (1971) 368–375.
[20] H. Buckley, On the radiation from the inside of a circular cylinder, Philos. Mag. 4 (1927) 753–762.
[21] Yu.N. Lyubitov, Calculation of the Interaction of Molecular Flows with Surrounding Vessels, Nauka, Moscow, 1964.
[22] A.I. Ivanovsky, Some questions of interaction of measuring cavity with a flow of rarefied gas, Trudy TsAO 56 (1964) 49–96.
[23] W.C. De Marcus, The influence of specular reflection on the Knudsen conductance of circular capillaries, in: Advances in Applied Mechanics, Suppl. 1, Rarefied Gas Dynamics, Academic Press Inc., New York, 1961, pp. 161–168.
[24] W. Strieder, S. Prager, Upper and lower bounds on Knudsen flow rates, J. Math. Phys. 8 (3) (1967) 514–517.
[25] J. Pao, J. Tchao, Knudsen flow through a long circular tube, Phys. Fluids 13 (2) (1970) 527–528.
[26] F. Sharipov, V. Seleznev, Data on internal rarefied gas flows, J. Phys. Chem. Ref. Data 27 (3) (1998) 657–706.
[27] B.B. Dayton, Gas flow patterns at entrance and exit of cylindrical tubes, in: Proceedings of the Nat. Symp. Vac. Tech, Pergaman Press, London, New York, Paris, 1957, pp. 5–11.
[28] I.G. Neudachin, B.T. Porodnov, P.E. Suetin, Formation of narrow molecular beams by cylindrical channels, Zh. Tekh. Fiz. 42 (5) (1972) 1069–1072.

[29] B.S. Ivanov, V.S. Troitsky, On formation of the directivity pattern of molecular beams, Zh. Tekh. Fiz. 33 (4) (1963) 494–499.

[30] G.F. Voronin, Directivity pattern of outflow of a dissociating gas from the Knudsen chamber, Zh. Fiz. Khim. 41 (7) (1967) 1663–1668.

[31] E.B. Gordon, A.N. Ponomarev, A choice of optimal parameters of multichannel formers of atomic beams, Zh. Tekh. Fiz. 40 (5) (1970) 1120–1126.

[32] P.G. Wahlbeck, T.E. Phipps, Effusion. II. Angular number distributions of gaseous cadmium from a right-circular cylindrical orifice into vacuum, J. Chem. Phys. 49 (4) (1968) 1603–1608.

[33] V.V. Levdansky, Control of mass transfer in application of thin layers of substances through deposition from a gas phase, in: Proceedings of International School-Seminar "Heat and Mass Transfer in Technology and Operation of Electronic and Microelectronic Systems": Part 2, Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1990, pp. 140–147.

[34] W.L. Winterbottom, Vapor–solid interactions and the effusion oven. II. Spatial distribution of an effusion flux, J. Chem. Phys. 49 (1) (1968) 106–116.

[35] V. Ruth, J.P. Hirth, The angular distribution of vapor flowing from a Knudsen cell, in: Proceedings of the International Symposium on Condensation and Evaporation of Solids, Gordon and Breach Science Publishers, New York, London, 1962, pp. 99–145.

[36] A.V. Luikov, T.L. Perelman, V.V. Levdansky, V.G. Leitsina, N.V. Pavliukevich, Theoretical investigation of vapour transfer through a capillary-porous body, Int. J. Heat Mass Transfer 17 (9) (1974) 961–970.

[37] V.V. Levdansky, N.V. Pavlyukevich, Kinetics of recondensation in a capillary, in: Problems of Theory of Transfer Processes, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1977, pp. 77–83.

[38] G.E. Gorelik, V.V. Levdansky, V.G. Leitsina, N.V. Pavlyukevich, G.I. Rudin, Kinetics of mass transfer with phase transformations in nonisothermal channels, in: Problems of Heat and Mass Transfer—77, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1977, pp. 39–40.

[39] N.V. Pavlyukevich, G.E. Gorelik, V.V. Levdansky, V.G. Leitsina, G.I. Rudin, Physical Kinetics and Transfer Processes in Phase Transitions, Begell House, Inc., New York, 1995.

[40] V.V. Levdansky, Characteristic features of mass transfer in a free-molecular gas flow, in: Proceedings of the Fourth National Congress on Theoretical and Applied Mechanics, Varna, 1981, pp. 778–782.

[41] V.V. Levdansky, V.G. Leitsina, Influence of the nonisothermicity of the surface of phase transition on formation of molecular beams and vacuum deposition of films, Preprint No. 21, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1990.

[42] V.V. Levdansky, V.G. Leitsina, An angular distribution of particles outgoing from a cylindrical channel with an evaporating inside surface, Zh. Tekh. Fiz. 61 (5) (1991) 134–136.

[43] V.V. Levdansky, Phase transformations in a capillary and nonequilibrium conditions of heat and mass transfer on a capillary porous body, in: Heat and Mass Transfer: Physical Foundations and Methods, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1979, pp. 20–21.

[44] V.V. Levdansky, Hoang Van Viet, Flow of a rarefied gas in a channel with account for phase transformations on its surface, in: Proceedings of International School-Seminar "Kinetic Theory of Transfer Processes in Evaporation and Condensation", A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1991, pp. 60–67.

[45] V.V. Levdansky, N.V. Pavlyukevich, Hoang Van Viet, Influence of phase transitions on the angular distribution of particles outgoing from a cylindrical channel, Inzh.-Fiz. Zh. 63 (3) (1992) 326–332.

[46] V.V. Levdansky, V.G. Leitsina, Hoang Van Viet, Vacuum deposition of particles escaping from a cylindrical channel with evaporating walls, in: Abstracts of Euromech Colloquim-285 "Kinetic Theory of Transfer Processes with Evaporation and Condensation," Minsk, 1991, pp. 18–21.

[47] V.V. Levdansky, Hoang Van Viet, Control of the angular distribution of the molecular beam escaping from a cylindrical channel, in: Heat and Mass Transfer in Phase and Chemical Transformations, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1990, pp. 143–150.

[48] V.V. Levdansky, Hoang Van Viet, Spatial distribution of energy and mass fluxes escaping from a cylindrical channel, Preprint No. 4, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of Belarus, Minsk, 1992.

[49] V.V. Levdansky, V.G. Leitsina, Hoang Van Viet, Spatial distribution of gas particles emerging from a nonisothermally heated cylindrical channel with heterogeneous processes on the surface, Int. J. Heat Mass Transfer 39 (5) (1996) 1103–1110.

[50] V.V. Levdansky, Control of substance deposition on the inside surface of a cylindrical channel, Inzh.-Fiz. Zh. 43 (4) (1982) 573–577.

[51] V.V. Levdansky, Influence of temperature distribution on condensation process in a capillary, in: Problems of Theory of Transfer Processes, A.V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of BSSR, Minsk, 1977, pp. 84–86.

[52] V.V. Levdansky, Formal kinetics of heterogeneous reaction in a cylindrical channel, Zh. Fiz. Khim. 68 (8) (1994) 1528–1529.

[53] V.V. Levdansky, J. Smolik, Kinetics of physical and chemical substance deposition from a gas phase in channels, Inzh.-Fiz. Zh. 74 (5) (2001) 142–145.

[54] V.V. Levdansky, J. Smolik, Influence of temperature distribution on chemical deposition in internal problems, Inzh.-Fiz. Zh. 76 (1) (2003) 142–145.

[55] B.V. Deryagin, I.G. Ershova, N.V. Churaev, Surface Forces in Thin Films and Disperse Systems, Nauka, Moscow, 1972.

[56] S.M. Gates, Surface chemistry in the chemical vapor deposition of electronic materials, Chem. Rev. 96 (4) (1996) 1519–1532.

[57] S. Chatterjee, C.M. McConica, Prediction of step coverage during blanket CVD tungsten deposition in cylindrical pores, J. Electrochem. Soc. 137 (1) (1990) 328–335.

[58] A. Nuriddin, J.R. Doyle, J.R. Abelson, Surface reaction probability in hydrogenated amorphous silicon growth, J. Appl. Phys. 76 (5) (1994) 3123–3129.

[59] H.Y. Kim, H.C. Kim, V.V. Levdansky, V.G. Leitsina, J. Smolik, Chemical deposition of substance from a gas phase in nonisothermal channels, Int. J. Heat Mass Transfer 43 (20) (2000) 3877–3882.

[60] D.C. Skouby, K.F. Jensen, Modeling of pyrolytic laser-assisted chemical vapor deposition: mass transfer and kinetic effects influencing the shape of the deposit, J. Appl. Phys. 63 (1) (1988) 198–206.

[61] P.A. Coon, P. Gupta, M.L. Wise, S.M. George, Adsorption and desorption kinetics for SiH_2Cl_2 on Si(1 1 1) 7×7, J. Vac. Sci. Technol. A 10 (2) (1992) 324–333.

[62] J.-L. Vassent, A. Marty, B. Gilles, C. Chatillon, Angular distribution of molecular beams and homogeneous layer growth: optimization of geometrical parameters in molecular beam epitaxy, Vacuum 64 (1) (2001) 65–85.