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International Journal of Heat and Mass Transfer 43 (2000) 3877–3882

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

# Chemical deposition of substance from gas phase in nonisothermal channels

H.Y. Kim[a], H.C. Kim[a], V.V. Levdansky[b,*], V.G.. Leitsina[b], J. Smolik[c]

[a]Korea Research Institute of Chemical Technology, Taejon 305 600, South Korea
[b]A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, Minsk 220072, Belarus
[c]Institute of Chemical Process Fundamentals of the Academy of Sciences of the Czech Republic, Prague 165 02, Czech Republic

Received 21 July 1999

**Abstract**

The possibility of using nonisothermality effect in filling semi-closed channels by means of deposition of gas molecules on the inner channel surface is analyzed. The case of chemical deposition is investigated for free-molecular gas flow in the cylindrical channel with the temperature-dependent coefficient which characterizes the efficiency of collisions of molecules with the surface. It is shown that decrease in the surface temperature from the bottom to the open end of the channel enables one to obtain both the substance film which is sufficiently uniform in thickness and the film with monotonous decrease in the thickness towards the exit from the channel. The last factor is important for the problem of filling the channel by the substance without formation of cavities. The possibility of realization of the above temperature distribution along the channel by means of the microwave radiation is considered. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Chemical deposition; Channels; Microwave radiation

## 1. Introduction

Deposition of a substance on the walls of channels of different shapes is known to be necessary for manufacturing a number of microelectronics elements [1]. Here it should be noted that two aspects can be distinguished in this problem. In some cases deposition of a uniform thin film is needed on the inner channel surface, in others there is a need to fill channels by substance without the appearance of a cavity which can arise as a result of more intensive deposition near the open ends of the channels. The questions of the chemical deposition of a substance from a gas phase in semi-closed channels of different shapes were discussed in [1–3]. It is shown, in particular, that uniformity in a forming layer increases with a decrease in the coefficient $\alpha$ characterizing the efficiency of collisions of molecules with the surface. The possibility for uniform deposition of substance in an open channel was considered for a symmetric case when the gas pressure is the same near both channel ends [4,5]. The temperature profiles have been found which should be created to realize uniform deposition. The cases of both physical and chemical deposition have been analyzed.

In the present paper, the possibility of using the

* Corresponding author. Tel.: + 37-517-2842250.
*E-mail address:* lvv@nsl.hmti.ac.by (V.V. Levdansky).

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PII: S0017-9310(00)00017-X

**Nomenclature**

$E_a$ activation energy of heterogeneous chemical reaction
$I$ dimensionless density of flux of reflected molecules
$I_r$ dimensionless density of resultant flux of molecules
$I^-$ dimensionless density of flux of incident molecules
$L$ channel length
$L_1$ plate thickness
$l$ dimensionless channel length ($l = L/r$)
$q$ power dissipated per unit volume
$R$ gas constant
$r$ channel radius
$T$ temperature
$X$ coordinate directed along the channel from the bottom
$x$ dimensionless coordinate directed along the channel ($x = X/L$).

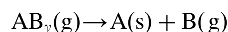
*Greek symbols*
$\alpha$ efficiency of collisions
$\sigma$ relative drop in flux density
$\omega$ angular frequency

*Subscripts*
i isothermal
L least
m monotonous
r resultant

nonisothermality effect is considered in the case of filling semi-closed cylindrical channels (i.e., the channels with one open end in contact with a gas phase) by means of chemical deposition of molecules from a gas phase on the inner channel surface. This process is often applied in the technology of manufacturing microelectronic elements. The possibility of obtaining thin coatings of a substance with the least thickness drop along the channel length is analyzed.

## 2. Formulation and solution of the problem

Consider chemical deposition of a substance on the walls of a semi-closed cylindrical channel of length $L$ and radius $r$ (Fig. 1). We suppose analogously to [6] that the molecules of gas $AB_\gamma$ collide with the heated surface and a chemical reaction takes place, resulting in the formation of the solid phase A and the gas B. This reaction can be written as



$$AB_\gamma(g) \rightarrow A(s) + B(g)$$

As an example of such a reaction, pyrolytic chemical deposition of nickel from nickel carbonyl is given in [6]. As noted in the above-mentioned paper, similar processes can be described by a first-order reaction. Let us use the coefficient which determines the efficiency of collisions of molecules with the surface, and which is equal to the ratio of the number of collisions leading to chemical reaction in accordance with the above-presented scheme to the total number of collisions of initial molecules with the surface. The coefficient $\alpha$ in the first-order reaction is related to the reaction rate constant [7] and can be written as

$$\alpha = \alpha_0 \exp\left\{-\frac{E_a}{RT}\right\} \quad (1)$$

where $E_a$ is the activation energy of heterogeneous chemical reaction, and the pre-exponential factor $\alpha_0$ can be considered constant due to its slight dependence on temperature.

Further, the flow regime in the channel is supposed to be free-molecular and the temperature is assumed to decrease linearly with the coordinate reckoned from the channel bottom:

$$T(X) = T(0)\left(1 + \beta\frac{X}{L}\right) \quad (2)$$

at a small relative temperature drop along the channel ($\beta < 0$ and $|\beta| \ll 1$). From Eqs. (1) and (2) we have the expression for $\alpha(x)$:

$$\alpha(x) = \alpha(0)\exp\{sx\} \quad (3)$$

where

$$s = E_a\beta/[RT(0)]. \quad (4)$$

In accordance with Eqs. (1)–(4) the value of $\alpha(0)$ with the constant quantities $\alpha_0$ and $E_a$ is related to the temperature $T(0)$ and, consequently, a change in $\alpha$ along the channel depends on the change in temperature.

It is obvious that the following formula can be writ-

ten for the dimensionless density of a flux of particles that are reflected elastically from the surface (the dimensional density is related to the density of molecular flux entering the channel through the open end):

$$I(x) = \left[1 - \alpha(x)\right] I^{-}(x). \tag{5}$$

Here the density of the molecular flux incident on the side surface $I^{-}$ includes the molecules reaching the given element of the surface from another part of the side surface and from the bottom, as well as through the open end. Distributions of the molecular fluxes reflecting from the surface and entering the open end are supposed to be described by the cosine law. We consider the problem in a quasi-steady approximation; the film thickness on the side channel surface is supposed to be much smaller than the channel radius, so that a change in the probabilities of molecular transitions from one element of the channel surface to another due to a change in the film thickness can be neglected.

The quantity $I^{-}$ is determined analogously to [8] in the form

$$I^{-}(x) = \int_0^1 I(\xi) K_1(|x-\xi|)\,\mathrm{d}\xi + I_0 K(x) + K(1-x) \tag{6}$$

where

$$I_0 = \left[1 - \alpha(0)\right]\left[2l \int_0^1 I(\xi) K(\xi)\,\mathrm{d}\xi + K_2(1)\right] \tag{7}$$

(we neglect, for simplicity, the dependence of the flux density $I_0$ of the molecules reflected from the channel bottom on the radial coordinate). In Eqs. (5) and (6) $K$, $K_1$, and $K_2$ are the functions characterizing the probabilities of the transitions of molecules from one element of the channel surface to another determined by following relations [7]:

$$K(x) = \frac{l^2 x^2 + 2}{2(l^2 x^2 + 4)^{1/2}} - \frac{l}{2}x, \quad K_1(x) = -\frac{\mathrm{d}K(x)}{\mathrm{d}x}, \quad \frac{\mathrm{d}K_2(x)}{\mathrm{d}x} = -2lK(x). \tag{8}$$

Substituting Eqs. (6) and (7) into Eq. (5) we obtain the following equation for $I(x)$:

$$I(x) = \left[1 - \alpha(x)\right] \int_0^1 I(\xi)\left\{K_1(|x-\xi|) + 2\left[1-\alpha(0)\right] \times lK(x)K(\xi)\right\}\mathrm{d}\xi + \left[1-\alpha(x)\right] \times \left\{K(1-x) + \left[1-\alpha(0)\right]K_2(1)K(x)\right\} \tag{9}$$

where $\alpha$ is determined in accordance with Eq. (3).

Eq. (9) was solved numerically for the different values of $l$ (5, 10), $\alpha$ (0) (0.001, 0.01, 0.1) and $s$ ($s \le 0$). According to Eq. (5), the density of the resultant flux of molecules on the wall is equal to

$$I_\mathrm{r} = I^{-} - I = \frac{\alpha}{1-\alpha} I. \tag{10}$$

Note that the quantity $I_\mathrm{r}$ is related to the thickness of the depositing layer and, respectively, characterizes the distribution of the layer thickness of molecules deposited along the channel.

## 3. Results and discussion

The results of calculations on the basis of Eqs. (9) and (10) show that in an isothermal case ($s = 0$) $I_\mathrm{ri}(x)$ is the monotonously increasing function. In the presence of nonisothermality, when temperature decreases from the channel bottom to the open end ($s < 0$), the function $I_\mathrm{r}(x)$ is nonmonotonous with a minimum and further with an increase in $|s|$ $I_\mathrm{r}(x)$ becomes a monotonously decreasing function. The dependence $I_\mathrm{r}(x)$ with different $s$ is illustrated in Fig. 2 for one of the cases considered.

Note that for a certain value of $s$ denoted as $s_\mathrm{L}$ the function $I_\mathrm{r}(x)$ characterized by the presence of minimum at $x = x_\mathrm{L}$ corresponds to the least relative drop $\sigma_\mathrm{L}$ in the resultant flux density along the channel ($\sigma_\mathrm{L} = [I_\mathrm{r}(0) - I_\mathrm{rL}]/I_\mathrm{r}(0)$ where $I_\mathrm{rL} = I_\mathrm{r}(x_\mathrm{L})$). In particular, the

Table 1
Values of parameter $s$, corresponding minimum drop of resultant flux density, and drop of resultant flux density for an isothermal case

| $l$ | $\alpha(0)$ | $-s_\mathrm{L}$ | $\sigma_\mathrm{L}$ | $\sigma_\mathrm{i}$ |
|---|---|---|---|---|
| 5 | 0.001 | 0.013 | 0.003 | 0.013 |
| 10 | 0.001 | 0.035 | 0.009 | 0.036 |
| 5 | 0.01 | 0.131 | 0.031 | 0.141 |
| 10 | 0.01 | 0.370 | 0.079 | 0.498 |
| 5 | 0.1 | 0.842 | 0.123 | 1.670 |
| 10 | 0.1 | 1.683 | 0.157 | 8.291 |

value $s_L = -0.37$ in Fig. 2 corresponds to the least drop $\sigma_L$. Table 1 contains such values of $s_L$ leading to the least drops in $I_r$, the corresponding values of $\sigma_L$, and the relative drops in the flux density for isothermal case $\sigma_i = [I_{ri}(1) - I_{ri}(0)]/I_{ri}(0)$ when $I_{ri}(x)$ is a monotonously increasing function.

It is seen from Table 1 that the nonisothermality decreases the value of $\sigma_L$ in comparison with $\sigma_i$ and the larger $l$ and $\alpha(0)$, the more noticeable this phenomenon. Thus, for $l = 10$, $\alpha(0) = 0.1$ we obtain $\sigma_i/\sigma_L \approx 52.8$ and for $l = 5$, $\alpha(0) = 0.001$ this ratio is equal approximately to 4.3. It follows from Table 1 that in the nonisothermal case with constant $\alpha(0)$ the deposition is more uniform for a smaller length of the channel $l$, and for a fixed $l$ the uniformity gets worse with an increase in $\alpha(0)$.

As was noted in the Introduction, besides uniform coverage of the walls of channels by a layer of substance deposited, in a number of cases a problem also exists concerning the filling of channels by substance without the appearance of cavities. This problem leads to the determination of a condition at which the function $I_r(x)$ begins to decrease monotonously to the open end of the channel. The values of $s_m$ and $\sigma_m$ (where $\sigma_m = [I_r(0) - I_r(1)]/I_r(0)$) corresponding to the appearance of a monotonous decrease in the function $I_r$ are presented in Table 2. In particular, $s_m = -0.6$ in Fig. 2 corresponds to this situation. It is seen from Table 2 that the qualitative dependence $\sigma_m$ on $l$ and $\alpha(0)$ has the same character as for $\sigma_L$.

The values of $s_L$ and $s_m$ from the Tables 1 and 2 allow one to find corresponding temperature drops along the channel. The values of the temperature drops are determined from Eq. (2) as a result of using these values of $s_L$ and $s_m$ and relation (4).

Let us estimate, as illustration, the relative temperature drop along the channel $\beta = [T(1) - T(0)]/T(0)$ corresponding to the beginning of monotonous decrease of the function $I_r(x)$ for the case of $E_a = 15{,}000$ cal/mole (such a value of the activation energy was used for calculations in [6]). Supposing that $\alpha(0) = 0.1$ corresponds to the temperature $T(0) = 1000$ K, we obtain for $l = 5$ the following relative temperature drops in terms of expressions (1)–(4) and of the values of $s_m$ from Table 2: $\beta = -0.002$, $-0.022$, $-0.139$ at $\alpha(0) = 0.001$, 0.01, 0.1, respectively. Note that the temperature drop increases with increase in $l$ and decreases with increase in $E_a$.

Thus, it is shown that in chemical deposition of sub-

Table 2
Values of parameter $s$ and corresponding minimum drop of the resultant flux density in the case of a monotonous decrease of $I_r$

| $l$ | $\alpha(0)$ | $-s_m$ | $\sigma_m$ |
|---|---|---|---|
| 5 | 0.001 | 0.025 | 0.012 |
| 10 | 0.001 | 0.065 | 0.028 |
| 5 | 0.01 | 0.223 | 0.092 |
| 10 | 0.01 | 0.600 | 0.226 |
| 5 | 0.1 | 1.053 | 0.227 |
| 10 | 0.1 | 1.902 | 0.258 |

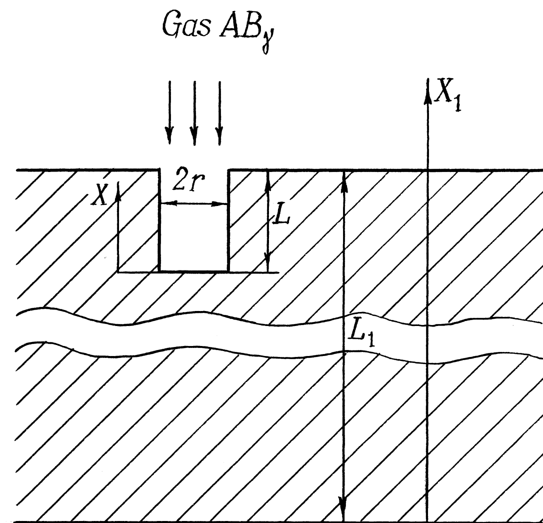



Fig. 1. Geometric scheme of the problem.

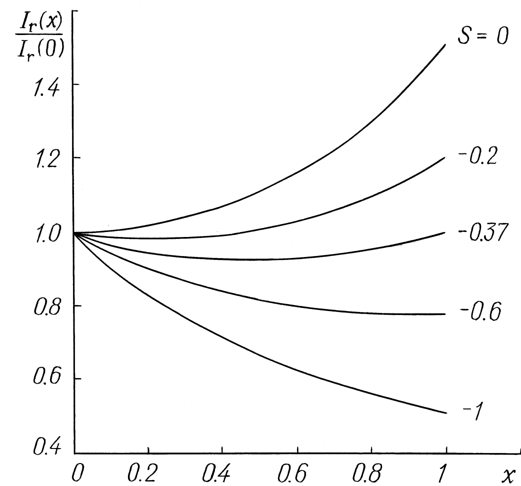



Fig. 2. Resultant flux density of deposited molecules as a function of the coordinate for $l = 10$, $\alpha(0) = 0.01$, and different values of $s$.

stance on the inner surface of the cylindrical channel the presence of temperature drop along the channel, when the bottom is heated more strongly than the open end, allows one to obtain both the substance film, which is sufficiently uniform in thickness, and a film with monotonous decrease in thickness. Decrease in the deposition rate towards the open end of the channel gives a possibility to fill the channel by substance without formation of a cavity, whereas in isothermal conditions the chemical deposition is more intense near the open end of the channel, which can result in channel "overgrowth" and formation of a cavity.

Let us discuss a possibility of realization of the above temperature distributions on the channel surface. Creation of such a distribution both on the walls of individual channels and in a multichannel system or in a porous body presents an independent problem. Use of the microwave radiation enables one to obtain inverse temperature gradients, when temperature inside a body exceeds the surface temperature [9,10].

Consider a plane–parallel plate of a dielectric material (Fig. 1), longitudinal dimensions of which substantially exceed its thickness $L_1$. The plate contains semi-closed channels of length $L$, which is much smaller than $L_1$, with the open channel ends emerging on the surfaces of the plate. The temperature distribution in the plate with influence of the microwave radiation for a stationary case is determined by the following equation [9]:

$$\lambda \frac{d^2 T}{dX_1^2} + q = 0 \tag{11}$$

where $\lambda$ is the effective heat conductivity supposed to be a constant quantity, $X_1$ is the coordinate reckoned from the plate surface and directed normally to it, $q$ is the power dissipated per unit volume and determined in accordance with the equation

$$q = \omega \varepsilon_0 \varepsilon''_{\text{eff}} E_{\text{rms}}^2$$

Here $\omega$ is the angular frequency, $\varepsilon_0$ is the permittivity of a free space, $\varepsilon''_{\text{eff}}$ is the effective relative loss factor, $E_{\text{rms}}$ refers to the r.m.s. electric field established within the dielectric.

The solution of Eq. (11) with symmetrical boundary conditions of the third kind for heat transfer on both surfaces is given as

$$\bar{T}(x_1) = T(x_1)/T_a = 1 + \frac{L_1 q}{2hT_a} + \frac{L_1^2 q}{2\lambda T_a} x_1(1 - x_1) \tag{12}$$

where $x_1 = X_1/L_1$, $T_a$ is the temperature of the surrounding medium, $h$ is the effective heat transfer coefficient (including radiative heat transfer at a sufficiently small difference between the temperatures of the plate surface and of the surrounding medium). Here an influence of the channels on conduction of heat is not taken into account.

It should be noted that the presence of the channels can change heat transfer conditons on the plate — surrounding medium boundary. This question was considered in [11].

It follows from Eq. (12) that the function $\bar{T}(x_1)$ is characterized by a maximum in the centre of the plate. Here with account for the inequality $L \ll L_1$ the temperature disribution in the channels can be approximated by a linear function, i.e. in the form of Eq. (2).

Thus, use of the microwave radiation allows one to realize, in principle, temperature distribution in a dielectric plate, for which the chemical deposition of the substance in the channels without formation of cavities is possible.

## 4. Conclusions

It is shown that with chemical deposition of substance on the inner surface of a cylindrical channel the presence of temperature drop along the channel, when the bottom is heated more strongly than the open end, allows one to obtain both the substance film, which is sufficently uniform in thickness, and a film with a monotonous decrease in thickness. Decrease in the molecular flux onto the side channel surface (and, accordingly, in the thickness of the depositing layer) enables one to fill the channel by substance without formation of a cavity. Use of microwave radiation gives a possibility to realize the temperature distribution in a dielectric plate, for which the chemical deposition of the substance in the channels with the above-mentioned characteristics takes place.

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