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GROWTH OF A METAL ISLAND FILM UNDER CONDITIONS OF NON-STEADY-STATE REEVAPORATION OF METAL ADATOMS

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Taking into account the non-steady-state reevaporation of adatoms, the article solves the problem of diffusion growth of a system of uniformly distributed nuclei of the metallic phase. An expression describing the kinetics of change of the zone of nuclei capture is obtained.

Investigations of the kinetics of the growth of nuclei of the metallic phase showed that at the initial stages the changes in the nuclei are determined solely by the diffusion sink flow of adatoms [1]. Under certain conditions it is even possible that accumulations of atoms are displaced. These results enable us to view condensation at the stage of growth of an island film as a diffusion problem and to use the obtained analytical expressions for describing the kinetics of deposition of metallic films. Among the large number of works dealing with this problem we can distinguish two trends. One examines steady-state problems [2, 3]. The solution of the steady-state diffusion equation is applicable only in the calculation of systems for which the condensation time is much longer than the life of the adatoms in the adsorbed state. This state occurs at high temperatures of the surface of the substrate when the reevaporation of the metal adatoms is of steady-state nature. The works belonging to the second trend solve the non-steady-state diffusion equation [4, 5] but reevaporation of metal adatoms is not taken into account, i.e., the case is described when

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$t \ll \tau_a$, which is possible when the temperature of the substrate is low or when the binding energy of the metal adatoms to the surface is large.

It should be pointed out that for a large number of systems, e.g., metal film–polymer, there is intense non-steady-state reevaporation at the initial stages [6].

The given case was examined in [7], and for describing it the authors used the non-steady-state diffusion equation taking the reevaporation of adatoms into account. The obtained solution for an isolated nucleus may be used for determining the kinetics of change in size only at the initial stages, when the distance between nuclei is larger than the radius of the zone of capture.

The present work examines a more general problem: the diffusion growth of a system of nuclei in the presence of non-steady-state reevaporation of metal adatoms.

We will assume that the surface of the substrate is homogeneous and isotropic. When there is no surface diffusion of the nuclei, changes in the concentration of adatoms with a view to reevaporation are described by an equation which has the following form in cylindrical coordinates [7]

$$\frac{\partial^2 n}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial n}{\partial \rho} - n + I\tau_a = \tau_a \frac{\partial n}{\partial t}. \tag{1}$$

We determine the boundary and initial conditions on the basis of the assumption that at the initial instant t = 0 there is already on the surface a critical concentration of metal adatoms, and that for $t \neq 0$ there exist always stable nuclei which are sinks for the adatoms. Then

$$n(\rho, 0) = n_{cr}, \; n(\rho_0, t) = 0. \tag{2}$$

It is obvious that for a system of nuclei uniformly distributed over the surface and having the same size, the concentration n has its maximum at points that are equidistant from the nuclei. The second boundary condition may therefore be written in the form

$$\left.\frac{\partial n}{\partial \rho}\right|_{\rho = L/X} = 0. \tag{3}$$

We solve Eq. (1) with conditions (2) and (3) in the approximation $\rho_0 = \text{const}$, using the Laplace transform with respect to the variable t. After transformation of Eq. (1) we obtain

$$\frac{\partial^2 \bar{n}}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial \bar{n}}{\partial \rho} - (1 + P\tau_a)\bar{n} = \frac{I\tau_a}{P} - n_{cr}\tau_a.$$

We replace the variable $Z = i\rho\sqrt{1 + P\tau_a}$. Then

$$\frac{\partial^2 \bar{n}}{\partial Z^2} + \frac{1}{Z}\frac{\partial \bar{n}}{\partial Z} + \bar{n} = \frac{I\tau_a}{P}\frac{1}{1 + P\tau_a} + \frac{n_{cr}\tau_a}{1 + P\tau_a}. \tag{4}$$

Equation (4) is an inhomogeneous Bessel equation with complex variable. Its solution is written in the following way:

$$\bar{n}(Z, P) = C_1 J_0(Z) + C_2 Y_0(Z) + \frac{I\tau_a}{P}\frac{1}{1 + P\tau_a} + \frac{n_{cr}\tau_a}{1 + P\tau_a}.$$

To find the coefficients C_1 and C_2, we transform the boundary conditions

$$\bar{n}|_{\rho = \rho_0} = 0, \quad \left.\frac{\partial \bar{n}}{\partial \rho}\right|_{\rho = L/X} = 0. \tag{5}$$

With a view to (5), the solution of the transformed Eq. (4) assumes the form

$$\bar{n}(\rho, P) = \left[\frac{I\tau_a}{P}\frac{1}{1 + P\tau_a} + \frac{n_{cr}\tau_a}{1 + P\tau_a}\right] \times \left[1 - \left\{J_0\left(i\rho\sqrt{1 + P\tau_a}\right) Y_1\left(i\frac{L}{X}\sqrt{1 + P\tau_a}\right) - Y_0\left(i\rho\sqrt{1 + P\tau_a}\right) \times \right.\right.$$
$$\left.\left. \times J_1\left(i\frac{L}{X}\sqrt{1 + P\tau_a}\right)\right\}\left\{J_0\left(i\rho\sqrt{1 + P\tau_a}\right) Y_1\left(i\frac{L}{X}\sqrt{1 + P\tau_a}\right) - \right.\right.$$
$$\left.\left. - Y_0\left(i\rho_0\sqrt{1 + P\tau_a}\right) J_1\left(i\frac{L}{X}\sqrt{1 + P\tau_a}\right)\right\}^{-1}\right]. \tag{6}$$

To obtain the solution of $n(\rho, t)$ we carry out the inverse Laplace transform:

$$n(\rho, t) = \int_{\varepsilon-i\infty}^{\varepsilon+i\infty} \bar{n}(\rho, P) e^{Pt} dP. \tag{7}$$

The integrand is a one-valued function of the complex variable P and $\lim_{P\to\infty} \bar{n}(\rho, P) \to 0$. Consequently, the integral of (7) is equal to the sum of the remainders in the poles of the integrand.

Let us determine these poles. An analysis of (6) shows that poles of first order are the points $P = 0$ and $P = -1/\tau_\alpha$. In addition to that, the function $\bar{n}(\rho, P)$ has an infinite number of poles at the points where the function

$$F(P) = J_0(i\rho_0\sqrt{1+P\tau_a})\, Y_1\left(i\frac{L}{X}\sqrt{1+P\tau_a}\right) - J_1\left(i\frac{L}{X}\sqrt{1+P\tau_a}\right) Y_0(i\rho_0\sqrt{1+P\tau_a}) = 0. \tag{8}$$

Let the solution of Eq. (8) be the numbers P_μ correlated with the numbers ε_μ by the relation $\varepsilon_\mu = i\sqrt{1+P_\mu\tau_\alpha}$. We determine the remainders at these poles:

$$\operatorname{Res}\left[\bar{n}(\rho, P) e^{Pt},\ P = -\frac{1}{\tau_a}\right] = 0,$$

$$\operatorname{Res}[\bar{n}(\rho, P)\, e^{Pt},\ P = 0] = I\tau_a\left[1 - \frac{J_0(i\rho)\, Y_1\left(i\frac{L}{X}\right) - Y_0(i\rho)\, J_1\left(i\frac{L}{X}\right)}{J_0(i\rho_0)\, Y_1\left(i\frac{L}{X}\right) - Y_0 i\rho_0)\, J_1\left(i\frac{L}{X}\right)}\right], \tag{9}$$

$$\operatorname{Res}[\bar{n}(\rho, P)\, e^{Pt},\ P = P_\mu] = \pi\left(\frac{I\tau_a}{1+\varepsilon_\mu} - n_{cr}\right) \times \left[\frac{J_0(\varepsilon_\mu\rho_0)}{Y_1\left(\varepsilon_\mu\frac{L}{X}\right)} - \frac{Y_1\left(\varepsilon_\mu\frac{L}{X}\right)}{J_1(\varepsilon_\mu\rho_0)}\right]^{-1} \times \left[J_0(\rho\varepsilon_\mu)\, Y_1\left(\frac{L}{X}\varepsilon_\mu\right) - Y_0(\rho\varepsilon_\mu)\, J_1\left(\frac{L}{X}\varepsilon_\mu\right)\right] \exp\left[-\frac{(1+\varepsilon_\mu^2)}{\tau_a} t\right].$$

Then, with a view to (9), the solution of Eq. (1) has the form

$$n(\rho, t) = \pi\sum_{\mu=1}^{\infty}\left(-\frac{I\tau_a}{1+\varepsilon_\mu} + n_{cr}\right)\left[\frac{Y_0(\varepsilon_\mu\rho_0)}{Y_1\left(\varepsilon_\mu\frac{L}{X}\right)} - \frac{Y_1\left(\varepsilon_\mu\frac{L}{X}\right)}{Y_0(\varepsilon_\mu\rho_0)}\right]^{-1} \times$$

$$\times\left[J_0(\rho\varepsilon_\mu)\, Y_1\left(\frac{L}{X}\varepsilon_\mu\right) - Y_0(\rho\varepsilon_\mu)\, Y_1\left(\frac{L}{X}\varepsilon_\mu\right)\right] \times \exp\left[-\frac{(1+\varepsilon_\mu^2)\, t}{\tau_a}\right] + I\tau_a\left[1 - \frac{J_0(\rho) K_1\left(\frac{L}{X}\right) + J_1\left(\frac{L}{X}\right) K_0(\rho)}{J_0(\rho_0) K_1\left(\frac{L}{X}\right) + J_1\left(\frac{L}{X}\right) K_0(\rho_0)}\right]^{-1}. \tag{10}$$

In order to simplify expression (10), we expand the last term into a series with respect to the functions $J_0(\rho\varepsilon_\mu)\, Y_1\left(\frac{L}{X}\varepsilon_\mu\right) - Y_0(\varepsilon_\mu\rho)\, J_1\left(\frac{L}{X}\varepsilon_\mu\right)$. After the respective transformations we obtain

$$n(\rho, t) = \pi\sum_{\mu=1}^{\infty}\left[\frac{Y_0(\rho_0\varepsilon_\mu)}{Y_1\left(\frac{L}{X}\varepsilon_\mu\right)} - \frac{Y_1\left(\frac{L}{X}\varepsilon_\mu\right)}{Y_0(\rho_0\varepsilon_\mu)}\right]^{-1}\left[J_0(\rho\varepsilon_\mu) \times\right. \tag{11}$$

$$\left.\times\, Y_1\left(\frac{L}{X}\varepsilon_\mu\right) - Y_0(\rho\varepsilon_\mu)\, J_1\left(\frac{L}{X}\varepsilon_\mu\right)\right] \times \left[\left(n_{cr} - \frac{I\tau_a}{1+\varepsilon_\mu^2}\right)\exp\left(-\frac{(1+\varepsilon_\mu^2)\, t}{\tau_a}\right) + \frac{I\tau_a}{1+\varepsilon_\mu^2}\right].$$

The obtained expression describes the dependence of the concentration of metal adatoms on the distance to the center of the nucleus, and it is the solution of the problem of diffusion growth of nuclei with more general initial and boundary conditions. As special cases,

the known expressions may be obtained from it. For instance, with steady-state diffusion, when $t \gg \tau_a$, the relation presented in [8] follows from (10). The solution of the problem of diffusion growth of a system of nuclei, examined in [5], is obtained from (11) if we put $\tau_a \gg t$.

Using (11), we determine the expression for the zone of capture of nuclei where the adatoms inevitably condense when they reach it.

If the reevaporation of adatoms from the zone of capture may be neglected, then as was shown in [3], we can write $A(\rho_0, t)=\pi X^2\left[\rho_0^2+\frac{2}{I\tau_a}\rho_0\left(\frac{\partial n}{\partial \rho}\right)_{\rho=\rho_0}\right]$. Then

$$A(\rho_0, t)=4X^2\sum_{\mu=1}^{\infty}\left[1-\frac{Y_0(\rho_0\varepsilon_\mu)}{J_1\left(\frac{L}{X}\varepsilon_\mu\right)}\right]^{-1}\left\{\left(\frac{n_{cr}}{I\tau_a}-\frac{1}{1+\varepsilon_\mu^2}\right)\exp\left[-\frac{(1+\varepsilon_\mu^2)t}{\tau_a}\right]+\frac{1}{1+\varepsilon_\mu^2}\right\}+\pi R^2. \quad (12)$$

We want to point out that the zone of capture is linearly correlated with the condensation coefficient $K = NA(\rho_0, t)$, and its change determines the nature of the reevaporation of the adatoms.

Since the diffusion processes of the adsorbed atoms and the size of the zone of capture determine the change in size of the nucleus, it is possible to evaluate the kinetics of their growth. For the case of three-dimensional condensation $dn = aX^3\rho_0^2\frac{1}{V_0}d\rho_0$. However, $dn = IA(\rho_0, t)dt$. Then the expression describing the kinetics of the growth of nuclei can be determined from the equation

$$aX^3\frac{1}{V_0}\rho_0^2 d\rho_0 = IA(\rho_0, t)dt. \quad (13)$$

If data are available on the parameters of a growing film, measured, e.g., by methods of electron microscopy, then expressions (11) and (12) can be used for determining the technological regimes of depositing a metal phase with the required sizes of nuclei. This calculation takes more fully into account the processes of non-steady-state reevaporation of adatoms taking place in the deposition of metals. Of particular interest are the obtained relationships when the effects of interaction of streams of metal atoms with the surface are used for studying its physicochemical properties [9]. In this case expressions (12) and (13) make it possible to use numerical methods for determining parameters such as τ_a and X, correlated in particular by known relationships with the surface energy of the substrate.

NOTATION

n, surface concentration of metal adatoms, m^{-2}; $\rho = r/X$; r, distance between the center of a nucleus and a point on the surface, m; X, diffusion path of adatoms in time τ_a, m; τ_a, lifetime of atoms in the absorbed state, sec; I, density of the incident flux of atoms, $sec^{-1}\cdot m^{-2}$; $\rho_0 = R/X$; R, radius of a nucleus, m; L, half the distance between nuclei, m; n_{cr}, critical concentration of adatoms, m^{-2}; J_0, zero-order Bessel function of the first kind; Y_0, zero-order Bessel function of the second kind; J_1, first-order Bessel function of the first kind; Y_1, first-order Bessel function of the second kind; K_0, zero-order Bessel function of the imaginary argument of the first kind; K_1, zero-order Bessel function of the imaginary argument of the second kind; $A(\rho_0, t)$, size of the zone of capture of a nucleus, m^2; K, condensation coefficient; α, parameter dependent on the geometric shape of the nucleus; V_0, volume occupied by an atom in the nucleus, m^3; N, concentration of nuclei, m^{-2}.

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