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A MATHEMATICAL MODEL OF METAL FILMS DEPOSITION FROM PHOTOACTIVE COMPOUND SOLUTIONS ON SOLID-LIQUID INTERFACE

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Abstract. The kinetics of the growth of thin metal films from solutions of photoactive chemical coordination compounds irradiated by light at a certain wavelength has been theoretically investigated. In the framework of our mathematical model the time dependencies of the basic characteristics of the film growth process (size distribution function, density of nucleation, concentration of metal on the surface) have been computed. They proved to be in accordance with the experimental data. It is shown that the flux of metal (substance) from the solution onto the surface of the substrate can be derived from the stationary diffusion equation with the added term taking into account the influence of the photochemical substance source. It may be inferred that the variation of light intensity, in great range, keeps the kinetics of the process of film deposition out of the drastic changes.

1. INTRODUCTION

The processes of metal films formation and growth on solid substrates are of great importance from both theoretical and practical viewpoints [1]. In the papers [2-5], the process of obtaining Ag, Au, Cu films on flat quartz substrates in the solutions of photoactive chemical coordination compounds was investigated experimentally. The essence of this method is the following. Let us consider a solution of the coordination compound $[M^{z+}L_n]X_m$, where M^{z+} is the central metal atom (z^+ is the oxidation level); L denotes innersphere ligands; X denotes outersphere counterions. If ligand to metal charge transfer ($L \rightarrow M$) occurs in this compound, the irradiation of solution by light at the wavelength $\lambda = \lambda_{L \rightarrow M}$ results in the reduction of the metal atom. By carrying the irradiation on, the central metal atom can be reducted to the zeroth valence state. Thus, we can write the scheme of the entire process as

$$[M^{z+}L_n]X_m \xrightarrow{h\nu} M^0 + L^+ + X^-.$$

One should put the substrate to be deposited on the bottom of the vessel filled with the solution. If we direct a light beam from above, its intensity decreases according to the Lambert-Buger-Behr law (Fig. 1).

Zeroth valence metal atoms generated by light will diffuse towards the substrate and be adsorbed on it. When the critical concenteration of metal on the substrate surface is reached, the growth of new crystal metal phase starts.

It was noted in [2-5], that the essential feature of films obtained in this way is the narrow size distribution of grains in the film. In those papers, on the basis of the Volmer-Weber theory [6] the qualitative explanation of results was proposed. The process of formation and growth of a new phase on the surface is the complicated multistage one [7], and the Volmer-Weber theory does not provide any exact quantitative description.

In our opinion, the method described above is very constructive and interesting for problems of films growing. In this work, we investigated theoretically the time dependencies of the basic characteristics of the growing film, on the basis of modern film growth ideas, presented in the publications [1, 7].

2. FLUX OF METAL ATOMS ONTO THE SUBSTRATE

In this work, the initial stage of the film condensation on the solid substrate was investigated. The substrate is considered to be a homogeneous continuous surface. Thermal effects of crystallization and adsorption are neglected. Passing through the solution, the light interacts with molecules of coordination compounds. That results in the formation of zeroth valence metal atoms. The power of metal atoms source is given by

$$g(x) = I_0 \varphi \alpha \exp[-\alpha x], \qquad (1)$$

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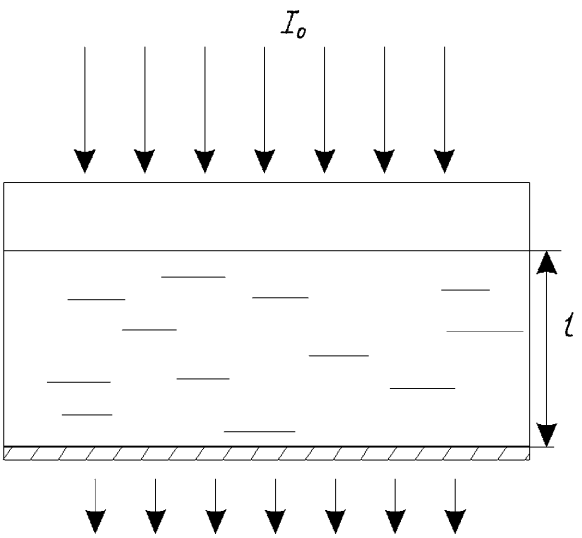

Fig. 1. The scheme of the process of photochemical film deposition; l — the thickness of the solution layer, I_0 — the incident light intensity.

where I_0 is the incident light intensity; α is the absorbtion coefficient; γ is the quantum yield. The absorption coefficient α can be represented by $\alpha = 2.3\varepsilon c_{complex}$, where ε is the extinction; $c_{complex}$ is the concentration of absorbing centres in the solution. Here, we suppose that $c_{complex}$ is constant. If the height of solution l (Fig. 1) is small, the probability of the formation of metal clusters in the bulk of solution (homogeneous nucleation) vanishes. In this case, the flux of metal onto the substrate can be derived from the 1D stationary diffusion equation written by

$$D\Delta c(x) + g(x) = 0, \tag{2}$$

where Δ denotes the Laplacian; D is the diffusion coefficient; the power of source is given by the Eq. 1. We make use of the stationary diffusion equation for the following reasons:

1. the source of metal atoms is stationary
2. we suppose that the characteristic time of photochemical reaction is much less than that of diffusion and, i.e. the photochemical reaction is not the ratelimiting stage.

The boundary conditions to the Eq. 2 are

$$\left.\frac{dc}{dx}\right|_{x=0} = 0, \tag{3}$$

$$c(l) = c_s^*. \tag{4}$$

It means that the flux of metal into the system at the upper boundary of solution (x=0) misses and the concentration of metal on the surface (x=l) is constant and equal to c_s^*.

In fact, some average time-dependent concentration of adsorbed atoms on the substrate exceeding c_s^* exists. It is the reduced difference of these concentrations being referred to as the supersaturation

$$\xi(t) = \frac{c_s(t) - c_s^*}{c_s^*}, \tag{5}$$

that is the driving force for the phase transformation on surface. However, due to the growth is carried out at room temperature and the solubility of metal is very low, the equilibrium concentration of metal c_s^* is also low. This results in formation of surface metal islands at small supersaturations. Therefore, following [1, 7, 8], we assume that the application of the boundary condition (4) is enough satisfactory. By differentiation of the solution of the Eq. 2 with the boundary conditions (3) and (4), we can derive the form of the flux of metal to the surface

$$J_s = I_0\varphi(1 - \exp(-\alpha l)). \tag{6}$$

3. METAL ISLANDS FORMATION PROCESSES

According to the paper [7], a process of new phase formation goes through three basic stages. The first stage is the fluctuation formation of new phase nuclei. It is described by the Zeldovich theory, modified for the formation on the surface [7]. During this stage, the stationary flux of nuclei, which are spherical segments, has the form [7]:

$$I(\xi) = K(\xi + 1)\ln(\xi + 1)\exp\left(-\frac{b}{\ln^2(\xi + 1)}\right), \tag{7}$$

where ξ is the supersaturation; $b = (\sigma/(kT))^3 4\pi v$, σ is the surface tension; v is the volume per atom in nucleus; K is the proportionality coefficient depending on the duffusion coefficient of adatoms. The time lag is estimated by:

$$t_s = \frac{1}{-F''(n_{cr})W(n_{cr})}, \tag{8}$$

where n_{cr} is the number of atoms in critical nucleus; $F(n)$ is the Helmholtz energy of nucleus taking form of a spherical segment; $W(n)$ is the diffusion coefficient in the size space taking into account the probability of random eleminating or joining atoms to nucleus (the fluctuations of nucleus in the size space) [9].

$$F(n_{cr}) = \frac{b}{\ln(\xi + 1)} \tag{9}$$

At $t > t_s$ the second stage starts. This is the process of formation of new phase islands in the system. This stage is described by the system of equations:

$$\frac{\partial f(n;t)}{\partial t} + \frac{\partial (v(n;t) f(n;t))}{\partial n} = 0, \qquad (10)$$

where $v(n;t) \equiv \frac{dn}{dt}$ is the linear rate of nucleus growth, written as

$$v(n;t) = a\xi(t) n^{-m}, \qquad (11)$$

where a and m are coefficients depending on the mechanism of nuclei growth,

$$\frac{\xi_0}{\xi(t)} - 1 = \int_0^t J_s dt - k \int_0^t \int_{n_{cr}}^{\infty} f(n;t) n dn dt, \qquad (12)$$

where k is the coefficient depending on the metal under investigation. The equation above represents the matter conservation. The equation (10) should be complemented by the initial and boundary conditions [7, 10]

$$f(n;0) = 0, \qquad f(n_{cr};t) = \left. \frac{I(\xi(t))}{v(n;t)} \right|_{n=n_{cr}}. \qquad (13)$$

The method of solution of this equations system was developed in the paper [10]. The solution of the system allows us to derive the time dependencies of the basic characteristics of the film growth process:

1. the supersaturation $\xi(t)$ is as

$$\xi(t) = \xi_0 \frac{1}{1 + \frac{1}{\Gamma} T^k(t) \phi_k(T(t))} \qquad (14)$$

2. the frequency of nuclei formation $I(t)$ is as

$$I(t) = I(\xi_0) \frac{\exp[-T^k(t)\phi_k(T(t))]}{1 + \frac{1}{\Gamma} T^k(t) \phi_k(T(t))} \qquad (15)$$

3. the size distribution function $f(n;t)$ is as

$$f(n;t) = \frac{1}{k+1} n^{-\frac{k}{k+1}} \frac{I(\xi_0)}{\alpha \xi_0} \times \exp\left(-(T(t) - \frac{\rho(n)}{\alpha t_k \xi_0})^k \phi_k(T(t) - \frac{\rho(n)}{\alpha t_k \xi_0}) \right), \qquad (16)$$

where the auxillary function is $\rho(n) = \frac{n^{m+1} - n_{cr}^{m+1}}{m+1}$.

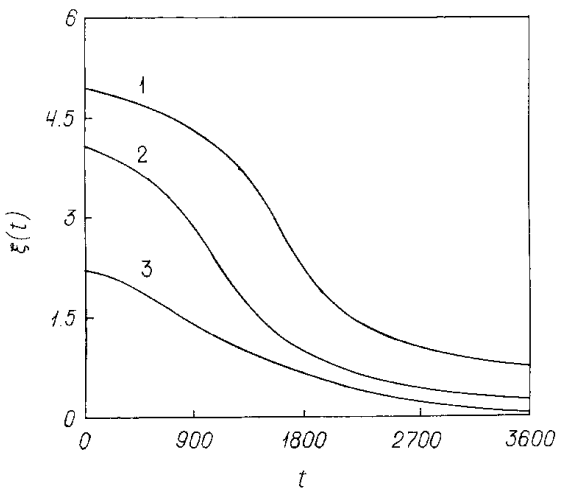

Fig. 2. The time dependence of supersaturation on the surface at different values of the incident light intensity: curve 1 — 10^{20} *quantum·m*$^{-2}$*·s*$^{-1}$; curve 2 — 10^{19} *quantum·m*$^{-2}$*·s*$^{-1}$; 3 — 10^{18} *quantum·m*$^{-2}$*·s*$^{-1}$; t — time (*s*), $\xi(t)$ — supersaturation (non-dimensional quantity).

The formulae (14–16) contain the parameter Γ – quantity, which is inverse with respect to the expansion small parameter. This parameter has the very important property: $\Gamma \approx n_{cr}$. All other symbols in these formulae correspond to those in the origin paper [10].

4. RESULTS OF CALCULATIONS AND CONCLUSIONS

Assuming that the growing film is determined by the following constants: $I_0 = 10^{20}$ *quantum·m*$^{-1}$*·s*$^{-1}$, $\gamma = 0.8$, $\alpha = 50$ *m*$^{-1}$, $l = 2 \cdot 10^{-4}$ *m* [2–5], $D = 10^{-9}$ *m*^{2}*·s*$^{-1}$, $\nu = 10^{-30}$ *m*^{3}, $c_s^* = 10^{20}$ *atoms·*m^{-2}, $\sigma = 1$ *J·m*$^{-2}$, $k = 1$, $a = 10^{14}$, $K = 10^{32}$, $\tau_r = 10^{-2}$ *s* [11], $S_{surf} = 10^{-4}$ *m*^{2}, $T = 298$ K .

Thus the value of the steady flux (Eq. 6) is $2 \cdot 10^{18}$ *atoms·m*$^{-2}$·s^{-1}. $n_{cr} \approx \Gamma = 53$. That criterium proves that the solution obtained by the small parameter method sufficiently describes the kinetics of the film growth. The time lag value is $t_s = 1.8 \cdot 10^{-6}$ *s*.

The results of calculations are presented in Figs. 2–5.

It is seen from Fig. 4, the size distribution takes the form of a bell. It is the form which is predicted by the theory [1, 7].

We have calculated the time dependencies of the size distribution function, the frequency of nucleation and the supersaturation on the surface at three different values of the incident light intensity of 10^{20}, 10^{19} and 10^{18} *quantum·m*$^{-1}$*·s*$^{-1}$. The variation of light intensity, in great range, keeps the kinetics of the process of film deposition out of the drastic changes.

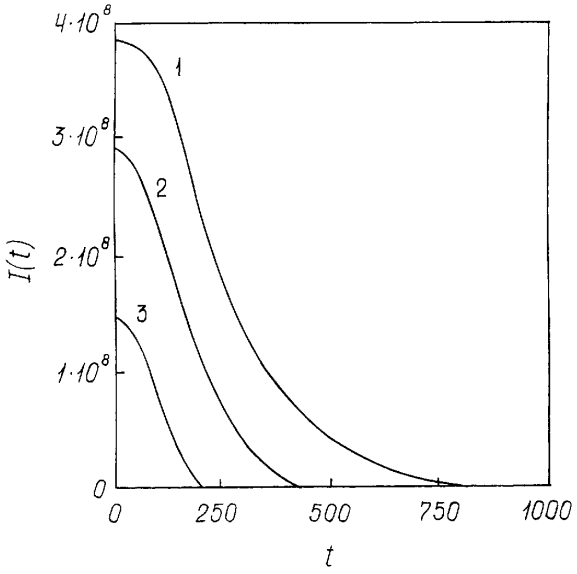

Fig. 3. The time dependence of nucleation frequency on the surface at different values of the incident light intensity: curve 1 — 10^{20} *quantum*·m^{-2}·s^{-1}; curve 2 — 10^{19} *quantum*·m^{-2}·s^{-1}; 3 — 10^{18} *quantum*·m^{-2}·s^{-1}; t — time (s), $I(t)$ — nucleation frequency (s^{-1}).

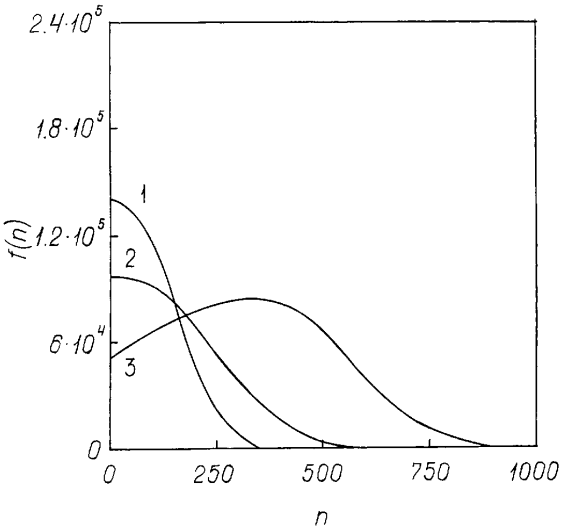

Fig. 4. The size distribution function at the incident light intensity of $I_0 = 10^{20}$ *quantum*·m^{-2}·s^{-1} and the irradiation time: curve 1 — 5 min; curve 2 — 10 min; curve 3 — 40 min; n — the number of nuclei (non-dimensional quantity), $f(n)$ — the size distribution function (non-dimensional quantity).

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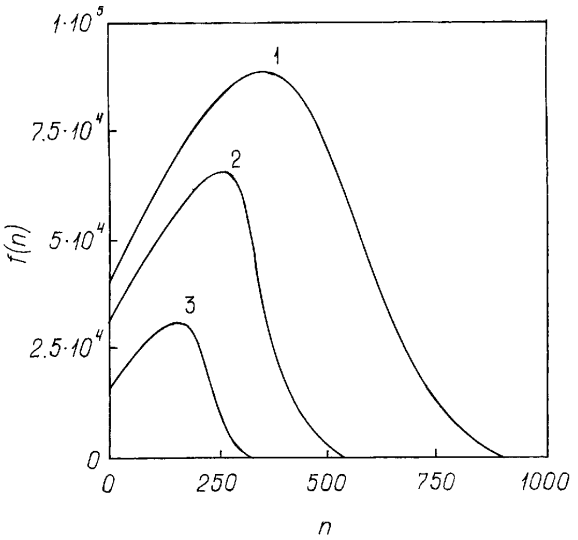

Fig. 5. The size distribution function at the irradiation time of 40 min and the incident light intensity: curve 1 — 10^{20} *quantum*·m^{-2}·s^{-1}; curve 2 — 10^{19} *quantum*·m^{-2}·s^{-1}; 10^{18} *quantum*·m^{-2}·s^{-1}; n — the number of nuclei (non-dimensional quantity), $f(n)$ — the size distribution function (non-dimensional quantity).

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