Металлофиз. новейшие технол. / Metallofiz. Noveishie Tekhnol.
2007, т. 29, № 2, сс. 249–266
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PACS numbers: 66.30.Dn, 72.10.Fk, 72.15.Qm, 73.40.-c, 73.50.Bk, 73.61.At

Influence of Diffusing Impurities on the Electrical Conductivity of Single-Crystal and Polycrystalline Metal Films

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The electrical-transport properties of thin single-crystal and polycrystalline metal films coated with an ultra-thin metallic layer of diffusing impurities are theoretically investigated. Analyzing changes of the electrical conductivity caused by the diffusion annealing, we investigate the processes of the bulk diffusion and the grain-boundary diffusion. Both the effective penetration depth of the diffusing atoms into the bulk of a sample and the penetration depth along the grain boundaries may be determined; the coefficients of bulk and grain-boundary diffusions may be estimated. The electrical conductivity is calculated within our model, and numerical analysis of the diffusion-annealing time dependence at various parameters is performed.

Теоретично проаналізовано провідність σ тонкої плівки з моно- та полікристалічною структурою, на одну із поверхонь якої нанесено дифундуючий ультратонкий шар іншого металу. Одержано точні та асимптотичні формули для коефіцієнта провідности і виконано докладний чисельний розрахунок залежности величини σ від часу дифузійного відпалювання за ріжних значень параметрів, які характеризують структуру зразка. Показано, що зміна провідности моно- та полікристалічного шару металу після дифузійного відпалу дає змогу дослідити власне процес об'ємної та зерномежової дифузії, визначити ефективну глибину проникнення атомів домішок в об'єм зразка і уздовж міжкристалічних меж та оцінити коефіцієнти об'ємної та зерномежової дифузії.

Теоретически проанализирована проводимость σ тонкой пленки с моно- и поликристаллической структурой, на одну из поверхностей которой нанесен диффундирующий ультратонкий слой другого металла. Получены точные и асимптотические выражения для коэффициента электропроводности и проведен детальный численный анализ зависимости величины σ от времени диффузионного отжига для различных значений параметров, характеризующих структуру образца. Показано, что изменение свойств проводимости моно- и поликристаллического слоя металла после диффузионного отжига позволяет исследовать сам процесс объемной и зернограничной диффузии, определить эффективную глубину проникновения атомов диффузата в объем образца и вдоль межкристаллитных границ и оценить коэффициенты объемной и зернограничной диффузии.

Key words: thin single-crystal metal layer, electrical conductivity, size-effects, bulk diffusion, grain-boundary diffusion.

(Received August 19, 2006)

1. INTRODUCTION

The size-effects in the electrical conductivity of finite-size conductors have been of interest for many years. As well-known, the electrical conductivity, σ, of a thin single-crystal metal layer of the thickness, d, which is much less the electron mean free path l_0, $d << l_0$, is proportional to the layer thickness, $\sigma \sim d$ (when the surface electron scattering is angle independent; it is the well-known Fuchs model [1] with the constant specular coefficient, q). In the case when the electron scattering by boundaries of the layer depends on the angle of incidence—the Falkovsky model (see Refs. [2] and [3]), the electrical conductivity σ is proportional to the square root of the layer thickness, $\sigma \sim \sqrt{d}$.

Let us discuss the case when one of the layer surfaces is coated with the ultra-thin metallic layer of diffusing impurities. It is well known that the characteristics of the electron transport in thin films may be changed essentially due to the coating with foreign atoms on to the film surface. Under the certain conditions of heat treating, impurity atoms may diffuse from the thin coating layer into the basic layer. As a result, in the case of single-crystal film, a region with an overconcentration of impurity atoms appears near the basic layer surface. Within the frameworks of the Fuchs model, the conductivity of the base layer becomes proportional to the $d - x_0$ (see Refs. [4–10]), where x_0 is the penetration depth of the impurity atoms into the bulk of the basic layer. (Within the frameworks of the Falkovsky model, $\sigma \sim \sqrt{d - x_0}$.) The value of x_0 is given as follows:

$$x_0 = d\left\{1 - \frac{\sigma(t_D)}{\sigma(0)}\right\}. \quad (1)$$

Here, t_D is the diffusion annealing time, $\sigma(0)$ is the electrical conductivity of the film before the annealing [1–3, 11], $\sigma(t_D)$ is the electrical conductivity of the film after the diffusion annealing, it will be analyzed below. If the value of x_0 is known, one may estimate the bulk diffusion coefficient, D_l, taking into account $x_0 \sim \sqrt{D_l t_D}$.

In the case of sufficiently low temperatures of the diffusion annealing of the polycrystalline film, when temperature $T < 0.38T_m$ (where T_m is the melting temperature), the processes of the bulk diffusion are almost 'frozen' and impurity atoms diffuse along the grain boundaries (see Ref. [12]). The impurity atoms are localized on the grain boundaries. These atoms change the boundary scattering properties and the grain-boundary resistance [13–16]. Consequently, the resistance of the polycrystalline film coated with impurity atoms may be changed essentially due to the annealing procedure. By measuring and comparing the electric conductivity before and after the diffusion annealing, we may estimate the depth of the penetration of the impurity atoms along the grain boundaries and calculate the grain-boundary diffusion coefficient D_b .

At large annealing times, the penetration depth of the impurity atoms is of the order of the film thickness, $x_0 \sim d$. In this case, to determine the bulk and grain-boundary diffusion coefficients, one should determine first the minimal diffusion annealing time, $t_{D\min}$, when the resistance of the film remains almost constant at $t_D > t_{D\min}$ (see Refs. [13–16]).

In this paper, we present a consistent theory of the electric conductivity of single-crystal and polycrystalline films coated with ultra-thin metallic layers of diffusing impurities. Our approach provides a simple relation between the changes of the electrical transport properties due to the annealing and the diffusion coefficients of the foreign impurities. It may be useful for the interpretation of the experimental data and estimation of the parameters of impurity diffusion in thin films.

Below, we assume that the thickness of the capped impurity layer, d_1, is much less than the thickness of the film, $d_1 \ll d$ and, therefore, its contribution to the total conductivity of the system is vanishing.

2. THE ELECTRICAL CONDUCTIVITY OF THIN METAL FILMS COATED WITH THE DIFFUSING IMPURITIES

Let us discuss the electrical conductivity of a thin metal film and let one of the surfaces of the film is coated with ultra-thin layer of the diffusing impurities. The foreign impurities diffuse either into the bulk of the film, see Fig. 1, *a* (when the basic film has a single-crystal structure) or along the grain boundaries, see Fig. 1, *b* (when the basic film has a polycrystalline structure). Let the x axis is directed down, normally to the film surface, and the x co-ordinate is counted from the upper boundary of the film, the y co-ordinate is directed along the film surface (see Figs. 1, *a*, *b*); let an external electric field $\mathbf{E} = = (0, E, 0)$ is directed along the film surface.

The electric current density $\mathbf{j}$ in the film is given as follows:

$$\mathbf{j} = -\frac{2e}{dh^3}\int_0^d dx \int d^3p \frac{\partial f_0}{\partial \varepsilon} \mathbf{v}\Psi(x, \mathbf{p}). \tag{2}$$

Here, $\Psi(x,\mathbf{p})$ is a non-equilibrium addition to the Fermi distribution function of electrons, $f_0(\varepsilon)$. Function $\Psi(x,\mathbf{p})$ obeys the linearized Boltzmann equation,

$$v_x \frac{\partial \Psi}{\partial x} + \frac{\Psi}{\tau(x,\mathbf{p})} = e\mathbf{v}\mathbf{E}, \tag{3}$$

where $e, x, \varepsilon, \mathbf{p}$ and $\mathbf{v}$ are the electron charge, co-ordinate, energy, quasi-momentum and velocity, respectively, h is the Planck constant.

In the case when distribution of the foreign impurity atoms deep into the film is inhomogeneous, the characteristic frequency of the bulk electron collisions, $\tau^{-1}(x,\mathbf{p})$, may be written as (see Refs. [9, 10])

$$\frac{1}{\tau(x,\mathbf{p})} = \frac{1}{\tau_0} + \frac{1}{\tau_1(x)} + \frac{1}{\tau_2(x,\mathbf{p})}, \tag{4}$$

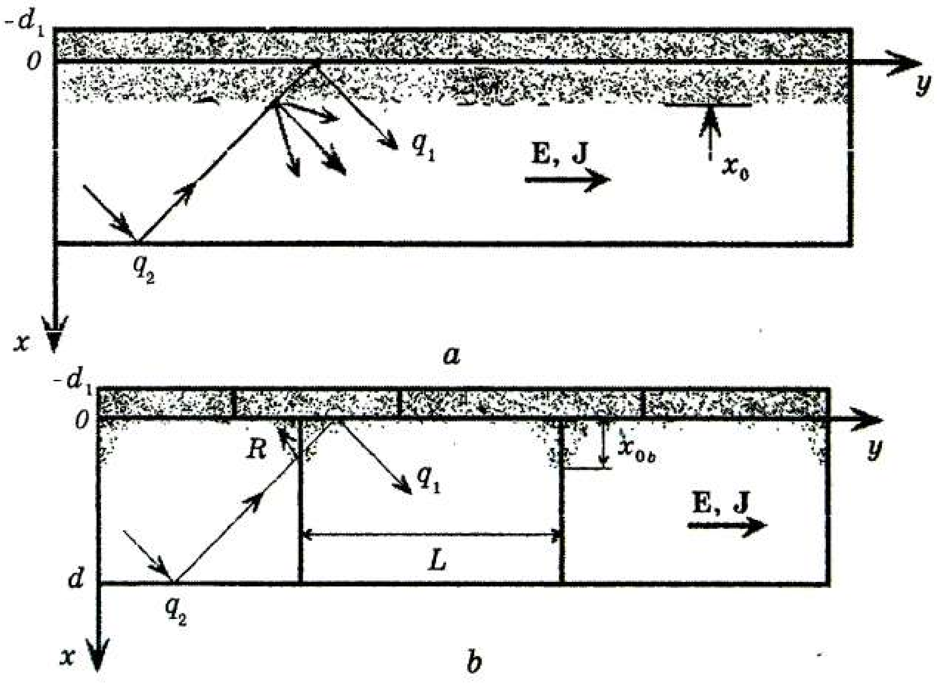


Fig. 1. Models of thin single-crystal (*a*) and polycrystalline (*b*) metallic films coated with ultra-thin layers of the diffusing impurities. The broken lines indicate schematically the possible electron trajectories.

where τ_0 is determined both by the electron-phonon collisions and by the collisions with residual impurities existed in the film before the annealing (it is assumed that τ_0 does not depend on the co-ordinate and momentum); $\tau_1(x)$ is determined by the electron scattering on the foreign impurity atoms which diffused into the bulk after the annealing; $\tau_2(x,\mathbf{p})$ is determined by the electron scattering at the grain boundaries, the transparency of which is affected by the migration of the foreign impurity atoms at low temperature annealing.

The general solution of Eq. (3) can be calculated according to

$$\Psi(x,\mathbf{p}) = F\exp\left\{-\frac{1}{v_x}\int_{x_s}^{x}\frac{dx'}{\tau(x',\mathbf{p})}\right\} + \frac{1}{v_x}\int_{x_s}^{x}dx' e\mathbf{v}\mathbf{E}\exp\left\{-\frac{1}{v_x}\int_{x'}^{x}\frac{dx''}{\tau(x'',\mathbf{p})}\right\}. \quad (5)$$

Here, $x_s = (0,d)$ is the co-ordinate of the scattering point on the film surface, F is determined by the boundary conditions.

For the scattering by surfaces of a film, it is assumed that a fraction q of the incoming electrons is scattered specularly, whereas the remainder is scattered diffusely (see Fuchs [1]). Lucas [11] generalized this approach for the case when upper and ground film surfaces scatter electrons in a different way:

$$\Psi^{s_i}\left((i-1)d,\mathbf{p}\right) = q_i(\mathbf{p})\Psi^{s_j}\left((i-1)d,\mathbf{p}'\right),\ i \neq j = 1, 2. \quad (6)$$

Here, quasi-momenta $\mathbf{p}$ and $\mathbf{p}'$ are related by the condition of specular reflection from the surface; $s_i = \operatorname{sign} v_x$ is the sign of the electron velocity component, v_x, which is normal to the surfaces $(s_1 = +,\ s_2 = -)$. The coefficient q_i determines the probability of specular reflection from the film surfaces when both the energy of electron and the tangential component of quasi-momentum $\mathbf{p}$ are conserved. The value of the coefficient q_i is taken to be angle-independent in the Fuchs model [1], whereas Falkovsky [2, 3] finds that q_i depends on the angle of incidence,

$$q_i = 1 - Q_i\frac{v_x}{v_0}. \quad (7)$$

Here, v_0 is the Fermi velocity of electrons, $Q_i = \text{const}$ depends on the average boundary roughness for the i-th film surface.

For the sake of simplicity, we assume that the Fermi surface is spherical with the radius p_0. In this case, there is no renormalization of the chemical potential of the reflected electrons and the corresponding terms are absent in Eq. (6) (see [17]).

Matching the functions $\Psi(x,\mathbf{p})$ at the film surfaces (by substituting Eq. (5) into Eq. (6)), we obtain a set of linear algebraic equations for the coefficient F whose solution allows us to determine $\Psi(x,\mathbf{p})$ and calculate the current density $\mathbf{J}$ (see Eq. (1)). Thus, we may calculate the conductivity of the thin metal film when foreign impurities are distributed inhomogeneously both inside the film and along the grain boundaries.

The calculation yields:

$$\sigma(t_D) = -\frac{2e^2}{d h^3} \int_{\upsilon_x>0} d^3p \frac{\partial f_0}{\partial \varepsilon} \frac{\upsilon_y^2}{\upsilon_x} \left\{ 2I + \frac{q_1 I_0^2 + q_2 I_d^2 + 2q_1 q_2 W(0) I_0 I_d}{1 - q_1 q_2 W(0)^2} \right\}, \quad (8)$$

$$I = \int_0^d dx W(x) \int_x^d dx' \, W^{-1}(|x'|), \; I_0 = \int_0^d dx W(0) W^{-1}(|x|), \; I_d = \int_0^d dx W(x), \quad (9)$$

$$W(x) = \exp\left\{ -\frac{1}{|\upsilon_x|} \int_x^d \frac{dx'}{\tau(x', \mathbf{p})} \right\}. \quad (10)$$

Here, $W(x)$ gives the probability that the charge carrier indeed reaches the surface without any additional scattering whereas the last scattering event was at x.

The subsequent results are determined essentially by the film structure, *i.e.* it is single-crystal or polycrystalline structure.

3. A SINGLE-CRYSTAL FILM AND THE EFFECT OF THE BULK DIFFUSION

Firstly, let us discuss the case when we may neglect by the electron scattering at the grain boundaries, *i.e.* $k \ll \alpha_0$ (see [18]) where $k \equiv d / l_0$, and α_0 is the grain-boundaries' parameter in the Mayadas–Shatzkes model [19]. We then have $\tau_2^{-1}(x, \mathbf{p}) = 0$ in Eq. (4), and $\tau_1^{-1}(x)$ may be written as (see [5, 7])

$$\tau_1^{-1}(x, t_D) = \upsilon_0 \sigma_{eff} n_0 C_l(x, t_D). \quad (11)$$

Here, σ_{eff} is effective cross-section of the electron scattering at the impurity atoms, n_0 is the bulk impurity concentration before the annealing, $C_l(x, t_D)$ is the distribution of the impurity atoms deep into the film. Note, this distribution depends essentially on the ratio between film thickness and the characteristic penetration depth of the impurity atoms.

In the case when considered film is thick enough (or the annealing time is sufficiently short), *i.e.* $d \gg \sqrt{D_l t_D}$, the coefficient of the bulk diffusion is constant $(D_l = \text{const})$, and there is no concentration discontinuity on the interlayer interface and impurity atomic solubility in the basic film is limited, the distribution of the impurity atoms deep into the film, $C_l(x, t_D)$, is given as follows [20]:

$$C_l\left(x,t_D\right)=C_{0l}\operatorname{erfc}\left(\frac{x}{2\sqrt{D_l\,t_D}}\right). \tag{12}$$

In the case when the basic film is thin enough (or annealing time is sufficiently large), *i.e.* $d \sim \sqrt{D_l\,t_D}$, the function $C_l\left(x,t_D\right)$ may be written as follows (see [20]):

$$C_l\left(x,t_D\right)=C_{0l}\left\{\frac{D}{1+D}+\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\left(\frac{n\pi D}{1+D}\right)\cos\left(\frac{n\pi x}{d\left(1+D\right)}\right)e^{-\frac{n^2\pi^2}{d^2(1+D)^2}D_l t_D}\right\}. \tag{13}$$

Here, $D=d_1/d$ and d_1 is the thickness of the layer of foreign impurities.

The integration on the Fermi surface in Eq. (8) yields the conductivity of the thin single-crystal film one of the surfaces of which is coated with diffusing impurities

$$\frac{\sigma\left(t_D\right)}{\sigma_0}=k^2\left\langle\frac{G\left(t_D\right)}{z^2\left(1-E\right)}\right\rangle, \tag{14}$$

$$G(t_D)=2J+\frac{q_1J_0^2+q_2J_d^2+2q_1q_2E\,W_l\left(0\right)J_0J_d}{1-q_1q_2E^2W_l\left(0\right)^2}, \tag{15}$$

$$J=\int_0^1 dxW_l\left(x\right)\int_x^1 dx'\,W_l^{-1}\left(\left|x'\right|\right)\exp\left\{-\frac{k}{z}\left(x'-x\right)\right\},$$

(16)

$$J_0=\int_0^1 dxW_l\left(0\right)W_l^{-1}\left(\left|x\right|\right)\exp\left\{-\frac{k}{z}x\right\},\quad J_d=\int_0^1 dxW_l\left(x\right)\exp\left\{-\frac{k}{z}\left(1-x\right)\right\},$$

$$W_l(x)=\exp\left\{-\frac{kA}{z}\left[\operatorname{erfc}\left(\frac{1}{\sqrt{t_l}}\right)-x\operatorname{erfc}\left(\frac{x}{\sqrt{t_l}}\right)+\sqrt{\frac{t_l}{\pi}}\left(\exp\left(-\frac{x^2}{t_l}\right)-\exp\left(-\frac{1}{t_l}\right)\right)\right]\right\},$$

(17)

$$W_l\left(x\right)=\exp\left\{-\frac{kA}{z}\frac{D}{1+D}\left[1-x+\frac{4}{\pi}\left(1+D\right)\sin\frac{\pi\left(1-x\right)}{2\left(1+D\right)}\cos\frac{\pi\left(1+x\right)}{2\left(1+D\right)}\times\right.\right.$$

$$\left.\left.\times\exp\left(-\frac{\pi^2t_l}{4\left(1+D\right)^2}\right)\right]\right\}, \tag{18}$$

$$E=\exp\left\{-\frac{k}{z}\right\},\quad A=l_0\sigma_{eff}n_0C_{0l},\quad t_l=\frac{4D_l}{d^2}t_D, \tag{19}$$

$$\langle \ldots \rangle = \frac{3}{4k} \int_0^1 dz \left(z - z^3\right)\left(1 - E\right)\left\{ \; \ldots \; \right\}. \tag{20}$$

Note here, $q_i = \text{const}$ within the frameworks of the Fuchs model, whereas the Falkovsky model assumed that $q_i = 1 - Q_i \cos\theta \equiv 1 - Q_i z$.

Equation (17) gives the probability that an electron will come the distance $[x, 1]$ without collisions within the assumption that metal layer is a semi-infinite medium for the foreign impurity atoms. Equation (18) takes into account finiteness of the metal film for the diffusing impurity atoms. Indeed, at large annealing time the exponential term in Eq. (13) is small, thus we may restrict ourselves by the first two terms [20], and $\sin(n\pi D / 1 + D) \cong n\pi D / 1 + D$.

Note, there are no foreign impurity atoms in the bulk of the film before the annealing. In this case, $\tau \equiv \tau_0$ and the result of (14) coincides with corresponding formulas either of Fuchs (if $q_1 = q_2 = q$) [1] or Lucas (if $q_1 \neq q_2$) [11] or Falkovsky [2, 3].

At short annealing time, t_D, the characteristic penetration depth of impurity atoms is much less the film thickness, $(D_l t_D)^{1/2} << d$. In this case, the derivative of the function $W_l(x)$ reaches its maximum value at $x = x_0 = a_l (D_l t_D)^{1/2}$ ($W_l''(x_0) = 0$). Because this function is a 'sharp' function of the x co-ordinate as to compare with the function $\exp\{-kx / z\}$ [5, 7], we may obtain asymptotical expressions of the integrals in Eq. (14) at $t_l << 1$.

Within the frameworks of the Fuchs model, we obtain the following:

$$\frac{\sigma(t_D)}{\sigma_0} \cong \begin{cases} 1 - \dfrac{3 l_0}{16(d - x_0)}(2 - q_2), & k >> 1, \\ \dfrac{3}{4}(1 + q_2)\dfrac{(d - x_0)^2}{d\, l_0} \ln\left(\dfrac{l_0}{d - x_0}\right), & k << 1. \end{cases} \tag{21}$$

When specular coefficient is taken to be angle-dependent (the Falkovsky model), we find

$$\frac{\sigma(t_D)}{\sigma_0} \cong \begin{cases} 1 - \dfrac{l_0}{10(d - x_0)}(1 + Q_2), & k >> 1, \\ \dfrac{3\pi}{4}\sqrt{\dfrac{2(d - x_0)}{l_0(1 + Q_2)}}, & k << 1, \end{cases} \tag{22}$$

$$x_0 = a_l \sqrt{D_l t_D}, \; a_l \approx 2 \ln^{1/2}\left\{2\sigma_{eff} n_0 C_{0l} \sqrt{D_l t_D}\right\}. \tag{23}$$

The asymptotical formulas (21) and (22) give us the possibility to find a relation between the characteristic depth of penetration of the impurity atoms into the bulk of the film, x_0, and change of the electrical conductivity due to the diffusion annealing, $\Delta\sigma = \sigma(0) - \sigma(t_D)$.

Taking for simplicity that boundary scattering is purely diffusive, we obtain for the Fuchs and Falkovsky models, respectively,

$$x_0 = d\frac{\Delta\sigma}{\sigma(0)} \cong d\frac{\Delta\sigma}{\sigma_0}\begin{cases}\left(\dfrac{3}{8k}\right)^{-1}, & k \gg 1,\\ \left(\dfrac{3}{2}k\ln\left(\dfrac{1}{k}\right)\right)^{-1}, & k \ll 1.\end{cases} \quad (24)$$

$$x_0 = d\frac{\Delta\sigma}{\sigma(0)} \cong d\frac{\Delta\sigma}{\sigma_0}\begin{cases}\left(\dfrac{1}{10k}\right)^{-1}, & k \gg 1,\\ \left(\dfrac{3\pi}{8}\sqrt{2k}\right)^{-1}, & k \ll 1.\end{cases} \quad (25)$$

On the other hand, within the frameworks of the τ-approximation model (11), the characteristic penetration depth of the impurity atoms is determined by Eq. (23), where the coefficient a_l depends both on the film characteristics and the coefficient of the bulk diffusion D_l. Note, at short annealing, the value of a_l varies very slowly as a function of the D_l [7, 8]. Consequently, a_l may be considered as a parameter and we obtain than the following formulas

$$D_l = \frac{d^2}{a_l^2 t_D}\left(\frac{\Delta\sigma}{\sigma(0)}\right)^2. \quad (26)$$

At large annealing time, the characteristic penetration depth of the impurity atoms is restricted by the film thickness and D_l may be written as (see [13–16])

$$D_l = \frac{d^2}{\pi^2 t_{D\min}}(1+D)^2. \quad (27)$$

Figures 2, *a–f* depict the annealing-time dependence of the electrical conductivity of the film coated with the diffusing impurities (in units of the bulk conductivity) at various parameters (annealing time is $t_l = t_D/4t_d$, where $t_d \equiv d^2/D_l$). Curves were calculated from Eq. (14) for the Fuchs and Falkovsky models of the boundary conditions in the cases when samples may be considered either as semi-infinitive half spaces (*a–c*) or films of the finite thickness (*d–f*). The following values of parameters were used: $Q_2 = q_2 = 0.5$, $A = 1500$, *1*—$Q_1 = 0.9$, $k = 1.0$, *2*—$q_1 = 0.1$, $k = 1.0$, *3*—$Q_1 = 0.9$, $k = 0.1$, *4*—$q_1 = 0.1$, $k = 0.1$ (*a*);

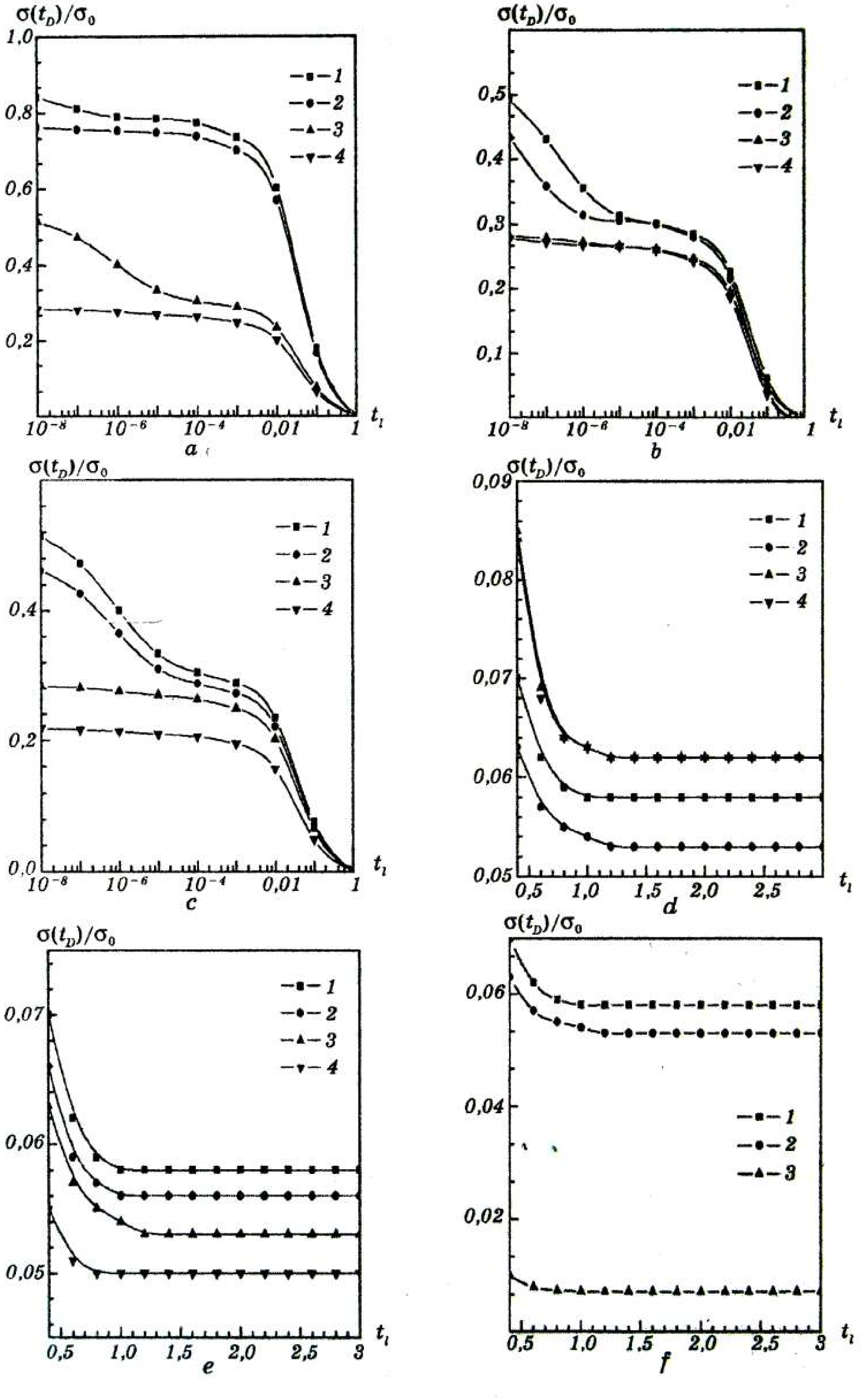

σ(t_D)/σ_0
1,0
0,8
0,6
0,4
0,2
10^-8
10^-6
10^-4
0,01
1
t_l
a
1
2
3
4
b
0,5
0,3
0,1
c
0,0
d
0,09
0,08
0,07
0,06
0,05
0,5
1,0
1,5
2,0
2,5
3
e
f
0,04
0,02

Fig. 2.

$Q_2 = q_2 = 0.5$, $k = 0.1$, *1*—$Q_1 = 0.9$, $A = 3000$, *2*—$Q_1 = 0.9$, $A = 9000$, *3*—$q_1 = 0.1$, $A = 3000$, *4*—$q_1 = 0.1$, $A = 9000$ (*b*); $A = 1500$, $k = 0.1$, *1*—$Q_1 = 0.9$, $Q_2 = 0.5$, *2*—$Q_1 = 0.9$, $Q_2 = 1.0$, *3*—$q_1 = 0.1$, $q_2 = 0.5$, *4*—$q_1 = 0.1$, $q_2 = 0.0$ (*c*); $Q_2 = q_2 = 0.5$, $A = 1500$, $D = 0.01$, *1*—$Q_1 = 0.9$, $k = 1$, *2*—$q_1 = 0.1$, $k = 1$, *3*—$Q_1 = 0.9$, $k = 0.1$, *4*—$q_1 = 0.1$, $k = 0.1$ (*d*); $A = 1500$, $k = 0.1$, $D = 0.01$, *1*—$Q_1 = 0.9$, $Q_2 = 0.5$, *2*—$Q_1 = 0.9$, $Q_2 = 1.0$, *3*—$q_1 = 0.1$, $q_2 = 0.5$, *4*—$q_1 = 0.1$, $q_2 = 0.0$ (*e*); $Q_2 = q_2 = 0.5$, $A = 1500$, $k = 0.1$, *1*—$Q_1 = 0.9$, $D = 0.01$, *2*—$q_1 = 0.1$, $D = 0.01$, *3*—$Q_1 = 0.1$, $D = 0.1$ (*f*).

We should note here that the annealing-time dependence of the conductivity of a thin film coated with diffusing impurities could be analyzed in the frames of the approximation of the average concentration [21] when an impurity distribution inside the film assumed to be uniform and it may be written as

$$C_{0l}\begin{cases}\operatorname{erfc}\left(\dfrac{1}{\sqrt{t_l}}\right)+\sqrt{\dfrac{t_l}{\pi}}\left(1-\exp\left(-\dfrac{1}{t_l}\right)\right), & t_l \ll 1,\\[2ex] \dfrac{D}{1+D}\left(1+\dfrac{2}{\pi}(1+D)\sin\dfrac{\pi}{1+D}\exp\left(-\dfrac{\pi^2}{4(1+D)^2}t_l\right)\right), & t_l \sim 1.\end{cases} \tag{28}$$

Integrating over the x co-ordinate in Eq. (14), we find for the Fuchs and Falkovsky models, respectively:

$$\frac{\bar{\sigma}(t_D)}{\sigma_0}=\frac{k}{\bar{k}}\left(1-\left\langle\bar{G}(t_D)\right\rangle\right)\cong\begin{cases}\dfrac{k}{\bar{k}}\left(1-\dfrac{3}{16\bar{k}}(2-q_1-q_2)\right), & \bar{k}\gg 1,\\[2ex] \dfrac{3}{4}\dfrac{(1+q_1)(1+q_2)}{1-q_1q_2}k\ln\dfrac{1}{\bar{k}}, & \bar{k}\ll 1,\end{cases} \tag{29}$$

$$\frac{\bar{\sigma}(t_D)}{\sigma_0}=\frac{k}{\bar{k}}\left(1-\left\langle z\bar{G}(t_D)\right\rangle\right)\cong\begin{cases}\dfrac{k}{\bar{k}}\left(1-\dfrac{Q_1+Q_2}{10\bar{k}}\right), & \bar{k}\gg 1,\\[2ex] \dfrac{3\pi}{4}k\sqrt{\dfrac{2}{\bar{k}(Q_1+Q_2)}}, & \bar{k}\ll 1,\end{cases} \tag{30}$$

where $\bar{G}(t_D)=\dfrac{2-q_1-q_2+(q_1+q_2-2q_1q_2)\bar{E}}{1-q_1q_2\bar{E}^2}$ and

$$\bar{G}(t_D)=\frac{Q_1+Q_2+(Q_1+Q_2-2Q_1Q_2z)\bar{E}}{1-(1-Q_1z)(1-Q_2z)\bar{E}^2}, \tag{31}$$

respectively;

$$\overline{\sigma_0} = \sigma_0 \frac{\bar{l}}{l_0}, \quad \overline{E} = \exp\left\{-\frac{\bar{k}}{z}\right\}, \quad \bar{k} = \frac{d}{\bar{l}}, \quad \bar{l}(t_D) = \frac{l_0}{1 + l_0\sigma_{eff} n_0 \overline{C}_l(t_D)}. \quad (32)$$

In Eqs. (29) and (30), the angular brackets are defined by Eq. (20) with the following substitution: $k \to \bar{k}$, $E \to \overline{E}$.

4. A POLYCRYSTALLINE FILM AND THE EFFECT OF THE GRAIN-BOUNDARY DIFFUSION

The effect of the grain-boundary diffusion on the conductivity of a thin polycrystalline film may be analyzed theoretically using the modified Mayadas–Shatzkes (MS) model [19]. The model use the following fact: in thin film the grains are not isotropic in form but they tend to grow in a 'columnar' fashion with column axis normal to the film axis (see Fig. 1, *b*). The grains, generally speaking, extended from the substrate to the top of the film and the only grain boundaries to be considered are those whose normals lie parallel to the film surface. We use the model, which takes into account those changes in the electron reflection at the grain boundaries, which caused by migration of the impurity atoms along the grains due to the annealing. This method of solving the problem on the annealing-time dependence of the conductivity of polycrystalline films was suggested early in Refs. [13–16].

The effective electron relaxation rate takes into account the bulk electron scattering and electron scattering at the grain boundaries and it may be written as (see [9, 14, 19])

$$\frac{1}{\tau(x, p_y)} = \frac{1}{\tau_0}\left\{1 + \alpha(x)\frac{p_0}{|p_y|}\right\}, \quad (33)$$

where p_0 is the Fermi quasi-momentum, the component p_y directed along the film surface and perpendicularly to the grain boundaries. Note, that Eq. (33) takes into account that the bulk diffusion is frozen at low temperature annealing, $\tau_1^{-1}(x) = 0$ (see [12]).

The grain-boundary parameter $\alpha(x)$ is a function of the x coordinate; this is due to the migration of the foreign impurity atoms along the grain boundaries. At low concentrations of the impurity atoms at the grain boundaries, $C_b(x, t_D) << 1$, we find that the probability of the electron scattering at the grain boundaries may be written as $R(x, t_D) = R_0 + \gamma_b C_b(x, t_D)$ (see [13–16]). We than obtain

$$\alpha(x) = \alpha_0 \frac{1 + (\gamma_b / R_0) C_b(x, t_D)}{1 - (\gamma_b / (1 - R_0)) C_b(x, t_D)}, \quad (34)$$

where $\alpha_0 = (l_0 / L)(R_0 / 1 - R_0)$ is the grain-boundary parameter of the

MS model before the annealing; L is the average crystallite size; R_0 is the probability of electron scattering by grain boundaries in the case when there are no impurity atoms at the boundaries; γ_b is the coefficient of the proportionality, it may has any sign. In the case when grain-boundary diffusion assists with the solid solution formation, $\gamma_b > 0$ [22], and the conductivity of the polycrystalline sample decreases due to increasing of the $R(x,t_D)$. In the opposite case, when impurity atoms cause the relaxation of elastic strains near the grain boundaries, $\gamma_b < 0$, and $R(x,t_D)$ decreases. Consequently, the conductivity of the polycrystalline sample increases [13–16].

In the case when $\sqrt{D_l t_D} \ll \delta$, where δ is the diffusion thickness of the grain boundary, one may neglect by the withdrawal of the foreign impurity atoms from the grain boundaries into the bulk of the sample [23], and consider the diffusion flow as 'one-dimensional' flow along the grain boundaries, deep into the film. Consequently, when the thickness of the film is at large enough and it is larger than characteristic penetration depth of the impurity atoms, β^{-1}, *i.e.* $d \gg \beta^{-1}$, the distribution of the impurity atoms deep into the film along the grain boundaries may be written as follows (see [24, 25]):

$$C_b(x,t_D) = C_{0b}\exp\{-\beta x\}, \tag{35}$$

$$\beta = \left\{\frac{2}{\delta D_b}\left(\frac{D_l}{\pi t_D}\right)^{1/2}\right\}^{1/2}, \tag{36}$$

where D_b is the grain-boundary diffusion coefficient.

Consequently, the integration of Eq. (8) with taking into account of the Eqs. (33)–(36) yields the following formulas of the conductivity of the polycrystalline film under the conditions of the grain-boundary diffusion

$$\frac{\sigma_b(t_D)}{\sigma_0} = k^2\left\langle\left\langle\frac{G_b(t_D)H^2}{z^2(1-E)}\right\rangle\right\rangle. \tag{37}$$

Here, function $G_b(t_D)$ is given by Eq. (15) with the following substitution: $W_l(x) \to W_b(x)$, where $W_b(x)$ may be written as

$$W_b(x) = \exp\left\{-\frac{k(H-1)}{z}\left[1 - x + \frac{\sqrt[4]{t_b}}{R_0}\ln\left(\frac{1-\frac{\gamma_b C_{0b}}{1-R_0}\exp\left(-\frac{1}{\sqrt[4]{t_b}}\right)}{1-\frac{\gamma_b C_{0b}}{1-R_0}\exp\left(-\frac{x}{\sqrt[4]{t_b}}\right)}\right)\right]\right\}, \tag{38}$$

$$H = 1 + \frac{\alpha_0}{\cos\varphi\sqrt{1-z^2}}, \quad t_b = \frac{\pi\delta^2 D_b^2}{4d^4 D_l} t_D. \tag{39}$$

The double angular brackets in Eq. (37) denote the integration over angle φ

$$\langle\langle\ldots\rangle\rangle = \frac{3}{\pi k}\int_0^{\frac{\pi}{2}} d\varphi \cos^2\varphi \int_0^1 dz \frac{(z-z^3)(1-E)}{H^2}\{\ldots\}. \tag{40}$$

In the case when considered film is thick enough, $(d/l_0) \to \infty$, the conductivity of the large-grain $(\alpha_0 << 1)$ or small-grain $(\alpha_0 >> 1)$ polycrystalline film may be written as [9, 10]

$$\frac{\sigma_b}{\sigma_0} \cong \begin{cases} 1 - \frac{3}{2}\alpha_0\left[1 + \frac{1}{\beta d R_0}\ln\left(1 + \gamma_b C_{0b}\frac{1-\exp(-\beta d)}{1-(R_0+\gamma_b C_{0b})}\right)\right], \alpha_0 << 1, \\ \frac{3}{4\alpha_0}\left[1 + \frac{1}{\beta d(1-R_0)}\ln\left(1 - \gamma_b C_{0b}\frac{1-\exp(-\beta d)}{R_0+\gamma_b C_{0b}}\right)\right], \alpha_0 >> 1. \end{cases} \tag{41}$$

Consequently, the characteristic depth of penetration of the impurity atoms along the grain boundaries x_{0b} is given by

$$x_{0b} = \beta = d\frac{\Delta\sigma_b}{\sigma_0}\begin{cases} \left|\frac{R_0(1-(1-R_0)/\gamma_b C_{0b})}{3/2\alpha_0}\right|, \alpha_0 << 1, \\ \left|\frac{(1-R_0)(1+R_0/\gamma_b C_{0b})}{3/4\alpha_0}\right|, \alpha_0 >> 1, \end{cases} \tag{42}$$

where $\Delta\sigma_b$ is change of the conductivity of the polycrystalline sample caused by the diffusion.

On the other hand, the characteristic penetration depth along the grain boundaries may be found from Eq. (38) assuming that function $W_b(x)$ reaches its extreme at x_{0b} (see [5, 7])

$$W_b''(x_{0b}) = 0 \text{ and } x_{0b}(t_D) = a_b\beta^{-1}(t_D), \quad a_b \cong \ln\left|\frac{\gamma_b C_{0b}}{\beta L}\right|. \tag{43}$$

Taking a_b as a task parameter at short annealing time, we obtain

$$D_b = \frac{d^2}{\delta a_b^2}\left(\frac{4D_l}{\pi t_D}\right)^{1/2}\left(\frac{\Delta\sigma_b(t_D)}{\sigma_b(0)}\right)^2, \tag{44}$$

where $\sigma_b(t_D)$ is given by Eq. (37), and $\sigma_b(0)$ is a conductivity of a thin polycrystalline film which was found in Refs. [19, 26].

Note, in the intermediate case, when the characteristic penetration depth is of the order of the film thickness, $\beta^{-1} \sim d$, the distribution of the impurity atoms along to the grain boundaries, according Refs. [13–16], may be found from Eq. (13) and the grain-boundary diffusion parameter may be estimated from Eq. (27).

To analyze the variation of the conductivity due to the migration of impurity atoms along the grain boundaries, we use the approximation of the average concentration. In this case, the impurity distribution along the grain boundaries assumed to be uniform and it may be written as

$$\overline{C}_b\left(t_D\right) = C_{0b}\sqrt[4]{t_b}\left(1 - \exp\left(-\frac{1}{\sqrt[4]{t_b}}\right)\right), \tag{45}$$

where t_b is given by Eq. (39). This assumption provides us the possibility to perform integration over co-ordinate in Eq. (37). As a result, we obtain the following:

$$\frac{\overline{\sigma}_b\left(t_D\right)}{\sigma_0} = T\left(\overline{\alpha}\right) - \left\langle\left\langle \overline{G}_b\left(t_D\right)\right\rangle\right\rangle, \tag{46}$$

$$\overline{H} = 1 + \frac{\overline{\alpha}}{\cos\left(\varphi\right)\sqrt{1 - z^2}},$$

$$\overline{E_b} = \exp\left(-\frac{k\overline{H}}{z}\right), \quad \overline{\alpha}\left(t_D\right) = \alpha_0 \frac{1 + \left(\frac{\gamma_b}{R_0}\right)\overline{C}_b\left(t_D\right)}{1 - \frac{\gamma_b}{1 - R_0}\overline{C}_b\left(t_D\right)}, \tag{47}$$

$$T\left(\overline{\alpha}\right) = 1 - \frac{3}{2}\overline{\alpha} + 3\overline{\alpha}^2 - 3\overline{\alpha}^3 \ln\left(1 + \frac{1}{\overline{\alpha}}\right) \approx \begin{cases} 1 - \frac{3}{2}\overline{\alpha}, & \overline{\alpha} \ll 1, \\ \frac{3}{4\overline{\alpha}}, & \overline{\alpha} \gg 1. \end{cases} \tag{48}$$

The function $\overline{G}_b\left(t_D\right)$ is given by Eq. (31) with the substitution $E \to \overline{E}_b$. The double angular brackets, analogously to Eq. (40), denote the averaging over angles with the substitutions $E \to \overline{E}_b$, $H \to \overline{H}$.

In the case when polycrystalline film is thick enough $(k \gg 1)$, the conductivity is given as follows (see also [18, 27]):

$$\frac{\overline{\sigma}_b\left(t_D\right)}{\sigma_0} = T\left(\overline{\alpha}\right) - \frac{3\left(2 - q_1 - q_2\right)}{16k} \times$$

$$\times\left\{1-\frac{32}{3\pi}\bar{\alpha}+12\bar{\alpha}^2+\frac{16}{\pi}\left[5-\left(4-5\bar{\alpha}^2\right)\Theta\left(\bar{\alpha}\right)\right]\bar{\alpha}^3-40\bar{\alpha}^4\right\}\cong$$

$$\cong\begin{cases}1-\dfrac{3}{2}\bar{\alpha}-\dfrac{3\left(2-q_1-q_2\right)}{16k}\left(1-\dfrac{32}{3\pi}\bar{\alpha}\right), & \bar{\alpha}\ll 1,\\ \dfrac{3}{4\bar{\alpha}}\left(1-\dfrac{2-q_1-q_2}{8k\bar{\alpha}}\left(1-\dfrac{512}{105\pi\bar{\alpha}}\right)\right), & \bar{\alpha}\gg 1,\end{cases} \tag{49}$$

$$\Theta\left(\bar{\alpha}\right)=\begin{cases}\dfrac{1}{\sqrt{1-\bar{\alpha}^2}}\ln\dfrac{1+\sqrt{1-\bar{\alpha}^2}}{\bar{\alpha}}, & \bar{\alpha}\le 1,\\ \dfrac{\arccos\left(\dfrac{1}{\bar{\alpha}}\right)}{\sqrt{\bar{\alpha}^2-1}}, & \bar{\alpha}>1.\end{cases}$$

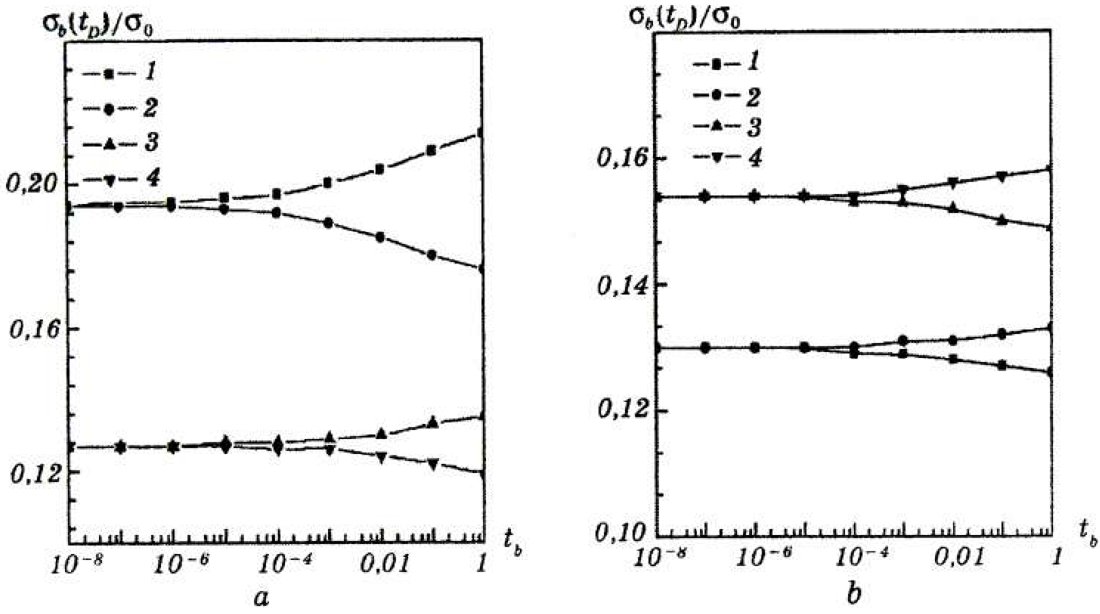
In the opposite case, when the considered polycrystalline film is thin $\left(k \ll 1\right)$, the conductivity is given by the following approximate formulas:

$$\frac{\bar{\sigma}_b\left(t_D\right)}{\sigma_0}\approx\frac{3}{4}\frac{\left(1+q_1\right)\left(1+q_2\right)}{1-q_1q_2}k\begin{cases}\ln\dfrac{1}{k}, & \bar{\alpha}\le k,\\ \ln\dfrac{1}{k}-\dfrac{4}{\pi}\bar{\alpha}, & \bar{\alpha}>k,\\ \ln\dfrac{1}{k\bar{\alpha}}, & \bar{\alpha}\ll\dfrac{1}{k}.\end{cases} \tag{50}$$

The conductivity of the polycrystalline film was calculated numerically and results are presented in Fig. 3. The conductivity is plotted against the dimensionless annealing time $t_b = \pi t_D t_\delta /(4 t_{db}^2)$ for various values of the task parameters in the case when the characteristic penetration depth of the impurity atoms is much less than the film thickness. Here, $t_\delta = \delta^2 / D_l$ is the characteristic electron diffusion time across the grain boundary and $t_{db} = d^2 / D_b$ is the characteristic electron diffusion time along the grain boundaries deep into the sample.

5. CONCLUSION

In summary, the coating of thin metallic films with ultra-thin layers of the diffusing impurities changes essentially the conductivity of the system after the annealing. We obtained a number of formulas, which allows us to find the coefficients of the bulk diffusion and the grain-boundary diffusion using simple experimental data. At short annealing



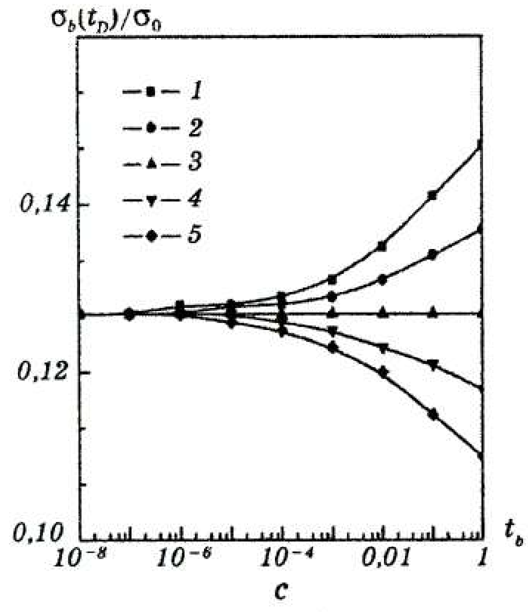


Fig. 3. Electrical conductivity of thin polycrystalline film as a function of the dimensionless annealing time, $t_b = \pi t_D t_\delta / (4 t_{db}^2)$, where $t_\delta = \delta^2 / D_l$ and $t_{db} = d^2 / D_b$. The following parameter values of were used: $q_1 = 0.1$, $q_2 = 0.5$, $C_{0b} = 0.1$, $\alpha = 3$, $R_0 = 0.5$, *1*—$\gamma_b = -0.5$, $k = 5.0$, *2*—$\gamma_b = 0.5$, $k = 5.0$, *3*—$\gamma_b = -0.5$, $k = 0.1$, *4*—$\gamma_b = 0.5$, $k = 0.1$ (*a*); $q_1 = 0.1$, $k = 0.1$, $C_{0b} = 0.1$, $\alpha = 2$, $R_0 = 0.5$, *1*—$\gamma_b = 0.3$, $q_2 = 0.0$, *2*—$\gamma_b = -0.3$, $q_2 = 0.0$, *3*—$\gamma_b = 0.3$, $q_2 = 0.5$, *4*—$\gamma_b = -0.3$, $q_2 = 0.5$ (*b*); $q_1 = 0.1$, $q_2 = 0.5$, $k = 0.1$, $C_{0b} = 0.1$, $\alpha = 3$, $R_0 = 0.3$, *1*—$\gamma_b = -1.0$, *2*—$\gamma_b = -0.5$, *3*—$\gamma_b = 0.0$, *4*—$\gamma_b = 0.5$, *5*—$\gamma_b = 1.0$ (*c*).

time, when the characteristic penetration depth of the foreign impurities is much smaller than the film thickness, it is enough to determine the changes of the electrical conductivity of the film caused by the diffusion annealing to estimate the values of the diffusion parameters.

In the opposite case, at large annealing time, when the characteristic penetration depth of the foreign impurities is of the order of the film thickness, to find the values of the diffusion coefficients from the experimental data, we need, firstly, to determine the minimal annealing time such as the following annealing procedure does not change the conductivity of the sample [13–16].

ACKNOWLEDGEMENTS

This work was partially supported by the Government Research Program of the Ministry of Ukraine for Education and Science, Reg. No. 0103U000773, 2003-2005. We gratefully acknowledge fruitful discussions with Prof. I. Yu. Protsenko.

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