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Influence of interdiffusion on the electrical conductivity of multilayered metal films

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Abstract: The annealing-time dependence of the electrical conductivity of multilayered single-crystal and polycrystalline metal films has been analyzed theoretically within the frame of the semi-classical approach. It is demonstrated that changes in the electrical conductivity which are caused by the diffusion annealing allow for investigating the processes of the bulk and grain-boundary diffusion, and for estimating the coefficients of the diffusion. The electrical conductivity was calculated and the numerical analysis of the diffusion-annealing time dependence was performed at various parameters.
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1 Introduction

Extensive applications of metallic multilayered films in electronics gave rise to a problem of stability of properties of multilayered elements. Therefore, diffusion processes in these films are of interest [1–11]. One possible way to obtain plausible information on the diffusion coefficients is to investigate the annealing-time dependence of kinetic coefficients in multilayered films showing the size effect (see, e.g. [2–11]). This is possibly due to the formation of a region with a high concentration of impurities diffused into the metal near the interface between the layers; these impurities cause the diffuse electron scattering. As a result, the positions of lines corresponding to the RF-size effects [2–4], the Sondheimer oscillations of the magnetoresistance [5, 6], etc. are shifted on the

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magnetic-field scale. They are determined not by the sample thickness d, but by the thickness of the impurity-free region $d - x_0$, where x_0 is the characteristic penetration depth of impurity atoms. The size-dependent magnetic phenomena mentioned above arise when an applied magnetic field is high enough, that the Larmour radius of electron trajectories is of the order of the sample thickness. Besides, to determine the bulk and the grain-boundary diffusion coefficients D_l and D_b, one may use the classical size effect in the conductivity of multilayered films. However, in this case, to obtain the information on the diffusion processes one needs to compare the experimental data and the annealing-time dependences of the electric conductivity calculated theoretically.

Note, we consider the case when the thicknesses of the layers,d_i, are less than the mean-free path of electrons but at that the thicknesses are much larger than the electron wave length. Thus, we may use the semi-classical approach to calculate an electron distribution function which obeys the Boltzmann transport equation. The previous theoretical investigations of the diffusing impurity effect on the conductivity also applied this approach for the cases of thin ($d \ll l_0$) single-crystal plates [4, 5] and thick ($d > l_0$) polycrystalline two-layered sample [7–9]. However, in Ref. [2–9] it was assumed that the thickness of one of the layers is negligibly small and, therefore, it merely plays the role of the source of diffusing atoms.

In this paper, the dependence of the conductivity of metallic multilayered films on the annealing time is calculated at arbitrary ratios between the layer thicknesses, crystallite sizes, and the mean-free path of electrons.

2 Conductivity of a double-layered film with account of interdiffusion

Let us consider a periodic multilayered structure consisting of the alternating metallic single-crystal (or polycrystalline) layers of different thicknesses ($d_i \neq d_j$) and different purities ($l_{0i} \neq l_{0j}$) (Fig. 1, a-b). Let the x-axis be directed normally to the interface. We assume that the film is of infinite extent in z and y directions. Therefore, the electrons move along the yz-plane in the same way as in a bulk metal. Let an external electric field $\mathbf{E} = (0, E_y, 0)$ be applied in parallel to the interface.

Taking into account that multilayered films are periodical structures with the bi-layer of the thickness $d = d_1 + d_2$ as a multilayer repeat period, we may reduce our problem and calculate the longitudinal conductivity of the two-layer film with the periodical boundary conditions. The conductivity of a multilayered film is given by the expression

$$\sigma = -\frac{2e}{dh^3} \sum_{i=1}^{2} \int_0^{d_i} dx \int d^3p \frac{\partial f_0}{\partial \varepsilon_i} v_{yi} \Psi_i \left(|x| , \mathbf{p} \right). \tag{1}$$

The non-equilibrium correction $-\frac{\partial f_0}{\partial \varepsilon_i} \Psi_i \left(x, \mathbf{p} \right)$ to the Fermi distribution function in the ith layer, $f_0 \left(\varepsilon_i \right)$, satisfies the Boltzmann kinetic equation linearized with respect to the electric field $\mathbf{E}$. Within the τ- approximation for the collision term, this equation takes

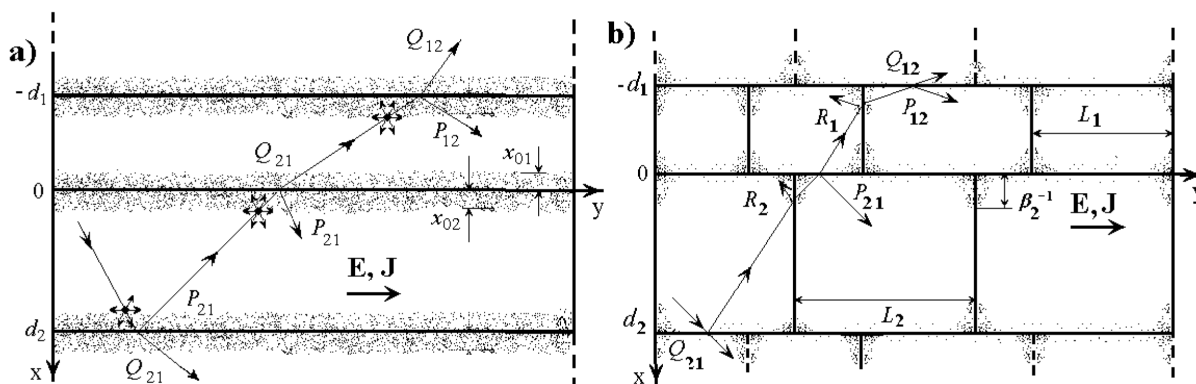

Fig. 1 Models of multilayer single-crystal (a) and polycrystalline (b) films in the presence of metal interdiffusion. The kinked-arrowed line shows schematically one of the possible trajectories of an electron being scattered in the impurity layer as well as at the interface between the layers.

the form

$$v_{xi}\frac{\partial \Psi_i}{\partial x}+\frac{\Psi_i}{\tau_i\left(x,\mathbf{p}\right)}=e\mathbf{v}_i\mathbf{E}. \tag{2}$$

Here, e is the electron charge, and ε_i and v_{yi}, are the energy and the velocity, respectively, of an electron in the ith layer, h is the Planck constant. The characteristic scattering rate in the bulk of the sample $\tau_i^{-1}\left(x,\mathbf{p}\right)$ may be represented in the following form [10, 11]

$$\tau_i^{-1}\left(x,\mathbf{p}\right)=\tau_{0i}^{-1}+\tau_{1i}^{-1}\left(x\right)+\tau_{2i}^{-1}\left(x,\mathbf{p}\right), \tag{3}$$

where $\tau_{0i}^{-1}=const$ is the$x$-independent frequency which is determined by electron collisions with phonons, whereas $\tau_{1i}^{-1}\left(x\right)$ describes the electron scattering at the impurities diffused into the bulk of the layer. The presence of the term $\tau_{2i}^{-1}\left(x,\mathbf{p}\right)$ in equation (3) corresponds to the electron scattering at the grain boundaries (when the grain-boundary diffusion is taken into account).

The general solution of Eq. (2) is given by

$$\Psi_i\left(x,\mathbf{p}\right)=F_i\exp\left\{-\frac{1}{v_{xi}}\int\limits_{x_s}^{x}\frac{dx'}{\tau_i\left(x',\mathbf{p}\right)}\right\}+\frac{1}{v_{xi}}\int\limits_{x_s}^{x}dx'e\mathbf{v}_i\mathbf{E}\exp\left\{-\frac{1}{v_{xi}}\int\limits_{x'}^{x}\frac{dx''}{\tau_i\left(x'',\mathbf{p}\right)}\right\}, \tag{4}$$

where x_s is the coordinate of the point where an electron scatters at the interlayer interface ($x_s=-d_1,0,d_2$). The solution (4) involves arbitrary coefficients F_i which are determined by the imposing of the boundary conditions.

Neglecting the edge effects, we may write the periodical boundary conditions which describe the interaction between the conducting electrons and the layer interfaces in the following form [12, 13]:

$$\Psi_i^{s_j}(s_id_i,\ \mathbf{p})=P_{ij}\Psi_i^{s_i}(s_id_i,\ \mathbf{p}')+Q_{ji}\tilde{\Psi}_j^{s_j}(s_id_i,\ \mathbf{p}''), \tag{5}$$

$$\Psi_i^{s_i}(0,\ \mathbf{p})=P_{ij}\Psi_i^{s_j}(0,\ \mathbf{p}')+Q_{ji}\Psi_j^{s_i}(0,\ \mathbf{p}''),\quad i\neq j=1,2. \tag{6}$$

Here, $P_{ij} = const$ is the probability of specular reflection of the electrons from the interface between ith and jth layers when the energy and the tangential (i.e., parallel to the interface) components of the electron quasi-momentum are conserved; $Q_{ji} = \text{const}$ is the probability of the electron transmission from jth layer into the ith layer without scattering. These parameters satisfy the following condition,$P_{ij} + Q_{ji} \leq 1$. The index $s_i = \text{sign } v_{xi}$ determines the sign of the x-component of the charge carrier velocity in the ith layer; v_{xi}, normal to the interface; quasi-momenta $\mathbf{p}$, $\mathbf{p}'$ and $\mathbf{p}''$ are related to each other by the condition of the specular reflection from the interface between the ith and jth layers. Symbol "tilde" in the second term in the right-hand side of Eq. (5) means that the given function describes the charge-carrier distribution in the layers which are adjacent to the bi-layer (the multilayer repeat period) which is considered. We assume that the Fermi surface in each layer is a sphere of radius p_0. Writing the boundary conditions (5) and (6), we omitted the terms corresponding to renormalization of the chemical potential of the reflected and transmitted electrons (see Ref. [13]).

By substituting functions $\Psi_i(x, \mathbf{p})$ from Eq. (4) into the boundary conditions (5) and (6), we obtain a set of linear algebraic equations that allows us to calculate the aforementioned coefficients F_i. With knowledge of the distribution function, one may calculate the conductivity of the metallic multilayered films in the presence of metal interdiffusion. The results of the further calculation depend essentially on whether the multilayered film has a single-crystal or a polycrystalline structure.

3 Bulk diffusion in multilayered single-crystal films

Let us discuss the case when either the average crystallite size, L_i, in each layer of the multilayered film is much larger than the mean-free path of charge carriers l_{0i}: $L_i \gg l_{0i}$ or crystallite boundaries are almost transparent for electrons, i.e. the probability of electron scattering by the grain boundaries is vanishing, $R_{0i} \ll 1$. In this case the grain-boundary parameter $\alpha_{0i} = \frac{l_{0i}}{L_i}\frac{R_{0i}}{1-R_{0i}}$ (see, Ref. [14]) satisfies the following inequality $\alpha_{0i} < d_i/l_{0i}$ and we may neglect the electron scattering by the grain boundaries [15, 16]. Thus, τ_{2i}^{-1} may be set equal to zero in Eq. (3) and $\tau_{1i}^{-1}(x)$ may be written in the following form [3, 4]

$$\tau_{1i}^{-1}(x) = v_0\,\sigma_{efi}\,n_{0i}\,C_{li}(x, t_D)\,. \tag{7}$$

Here v_0 is the Fermi velocity, σ_{efi} is the effective cross-section of electron scattering at the impurities, n_{0i} is the atom concentration in a pure sample.

Let us suppose that (i) the bulk diffusion coefficient is constant ($D_{li} = \text{const}$); (ii) there is no concentration jump at the layer interface and (iii) the metal solubility is limited. Then, at small annealing times, $\sqrt{D_{li}t_D} \ll d_i$, the distribution of impurity atoms, $C_{li}(x, t_D)$, in each layer of the bi-layer period is given approximately as (see, Ref. [17])

$$C_{l1}(x, t_D) = C_0\left\{\gamma_l - (1-\gamma_l)\,\text{erf}\frac{x}{2\sqrt{D_{l1}t_D}}\right\} \qquad x < 0, \tag{8}$$

$$C_{l2}(x, t_D) = C_0\gamma_l\text{erfc}\frac{x}{2\,\sqrt{D_{l2}t_D}}, \qquad x > 0, \tag{9}$$

where $\gamma_l = \frac{1}{1+\sqrt{D_{l2,1}}}$, $D_{l2,1} = \frac{D_{l2}}{D_{l1}}$, D_{li} is the coefficient of bulk diffusion in the ith layer of the bi-layer.

Calculating the distribution functions $\Psi_i(x, \mathbf{p})$ from Eq. (4) for each layer of the multilayer repeat period we obtain the following expression for the conductivity $\sigma(t_D)$ after the diffusion annealing

$$\sigma(t_D) = \frac{1}{d}\sum_{i=1}^{2} d_i \sigma_{0i} \Phi_i(t_D), \tag{10}$$

$$\Phi_i(t_D) = \frac{1}{2}k_i^2 \left\langle \frac{G_i(t_D)}{z^2(1-E_i)} \right\rangle, \tag{11}$$

where $E_i = \exp(-k_i/z)$, $k_i = d_i/l_{0i}$, $\langle\ldots\rangle = (3/2k_i)\int_0^1 d\,z\,(z-z^3)(1-E_i)\{\ldots\}$. The thickness-dependent function $\Phi_i(t_D)$ is determined both by the boundary scattering and the bulk collisions

$$\begin{aligned}
G_i(t_D) &= 2J_i + \frac{1}{\Delta(t_D)}\Big\{\Big(1 - P_{ji}^2 E_j^2 W_{lj}^2(0) - Q_{ij}Q_{ji}E_iE_j W_{li}(0)\, W_{lj}(0)\Big)\times\\
&\times\Big(P_{ij}\left(J_{di}^2 + J_{0i}^2\right) + Q_{ji}d_{j,i}\left(J_{di}J_{dj} + J_{0i}J_{0j}\right)\Big) +\\
&+ W_{li}(0)\,E_i\Big(P_{ij} + P_{ji}\left(Q_{ij}Q_{ji} - P_{ij}P_{ji}\right)E_j^2 W_{lj}^2(0)\Big)\times\\
&\times\left(2P_{ij}J_{di}J_{0i} + Q_{ji}d_{j,i}\left(J_{di}J_{0j} + J_{dj}J_{0i}\right)\right) + Q_{ji}E_jW_{lj}(0)\times\\
&\times\left(1 - \left(Q_{ij}Q_{ji} - P_{ij}P_{ji}\right)E_iE_jW_{li}(0)\,W_{lj}(0)\right)\times\\
&\times\left(2Q_{ij}J_{di}J_{0i} + P_{ji}d_{j,i}\left(J_{di}J_{0j} + J_{dj}J_{0i}\right)\right) + Q_{ji}E_jW_{lj}(0)\times\\
&\times\left(P_{ij}E_iW_{li}(0) + P_{ji}E_jW_{lj}(0)\right)\times\\
&\times\Big(P_{ji}d_{j,i}\left(J_{0i}J_{0j} + J_{di}J_{dj}\right) + Q_{ij}\left(J_{di}^2 + J_{0i}^2\right)\Big)\Big\},\\
\Delta(t_D) &= 1 - P_{ij}^2E_i^2W_{li}^2(0) - P_{ji}^2E_j^2W_{lj}^2(0) - 2Q_{ij}Q_{ji}E_iE_jW_{li}(0)\,W_{lj}(0) +\\
&+ \left(Q_{ij}Q_{ji} - P_{ij}P_{ji}\right)^2 E_i^2E_j^2W_{li}^2(0)\,W_{lj}^2(0),\\
d_{j,i} &= d_j/d_i,
\end{aligned} \tag{12}$$

$$\begin{aligned}
J_i &= \int_0^1 dx W_{li}(x)\int_x^1 dx' W_{li}^{-1}(|x'|)\exp\left(-\frac{k_i}{z}(x'-x)\right),\\
J_{d_i} &= \int_0^1 dx W_{li}(x)\exp\left(-\frac{k_i}{z}(1-x)\right),
\end{aligned} \tag{13}$$

$$J_{0i} = \int_0^1 dx W_{li}(0)\, W_{li}^{-1}(|x|)\exp\left(-\frac{k_i}{z}x\right). \tag{14}$$

Here, the function $W_{li}(x)$ gives the probability that an electron, that has started its movement in a point in the ith layer with the coordinate x,reaches the interface, $x_s = -d_1$ or d_2, without collisions with impurities diffused from the adjacent layers

$$W_{l1}(x) = \exp\left\{-\frac{k_1}{z}A_1\left[\gamma_l(1-x) - (1-\gamma_l)\left(erf\frac{1}{\sqrt{t_{l1}}} - x\,erf\frac{x}{\sqrt{t_{l1}}} + \right.\right.\right.$$
$$\left.\left.\left. + \sqrt{\frac{t_{l1}}{\pi}}\left(\exp\left(-\frac{1}{t_{l1}}\right) - \exp\left(-\frac{x^2}{t_{l1}}\right)\right)\right)\right]\right\}, \quad (15)$$

$$W_{l2}(x) = \exp\left\{-\frac{k_2}{z}A_2\gamma_l\left[erfc\frac{1}{\sqrt{t_{l2}}} - x\,erfc\frac{x}{\sqrt{t_{l2}}} - \right.\right.$$
$$\left.\left. - \sqrt{\frac{t_{l2}}{\pi}}\left(\exp\left(-\frac{1}{t_{l2}}\right) - \exp\left(-\frac{x^2}{t_{l2}}\right)\right)\right]\right\}, \quad (16)$$

$$A_i = l_{0i}\sigma_{efi}n_{0i}C_0, \quad t_{li} = \frac{4D_{li}}{d_i^2}t_D. \quad (17)$$

Before annealing, when $t_D = 0$, the diffusing impurities are absent in all layers of the multilayered structure and $C_{li}(x, t_D) = 0$. This allows us to perform integration over coordinates in Eqs. (13) and (14). The following expression for the conductivity can be obtained [18]

$$\sigma(0) = \frac{1}{d}\sum_{i=1}^{2} d_i\sigma_{0i}\Phi_i(0), \quad (18)$$

where σ_{0i} is the conductivity of a bulk sample and τ_{0i} is the corresponding relaxation time. In this case, the size effects in the electrical conductivity are determined mainly by the functions$\Phi_i(0)$ which depend on the thicknesses of the metal layers. Within our model we obtain the exact expressions for the thickness-depending functions$\Phi_i(0)$. When metal layers are thick (or thin) as to compare with the electron mean-free path we obtain

$$\Phi_i(0) = 1 - \langle G_i(0)\rangle \cong \begin{cases} 1 - \frac{3}{8k_i}\left(1 - P_{ij} - Q_{ji}\tau_{0j,i}\right), & k_i \gg 1, \\ \frac{3}{4}\frac{(1+P_{ij})(1-P_{ji}) + Q_{ij}Q_{ji} + 2Q_{ji}d_{j,i}}{(1-P_{ij})(1-P_{ji}) - Q_{ij}Q_{ji}}k_i \ln\frac{1}{k_i}, & k_i \ll 1. \end{cases} \quad (19)$$

$$G_i(0) = 1 - \frac{1}{\Delta(0)}\left\{(1+P_{ij}E_i)(1+P_{ji}E_j) - Q_{ij}Q_{ji}E_iE_j\right\}\left\{C_i(1-P_{ji}E_j) + Q_{ji}\tau_{0j,i}E_jC_j\right\}, \quad (20)$$
$$\Delta(0) = 1 - P_{ij}^2E_i^2 - P_{ji}^2E_j^2 - 2Q_{ij}Q_{ji}E_iE_j + (Q_{ij}Q_{ji} - P_{ij}P_{ji})^2E_i^2E_j^2,$$
$$C_i = P_{ij}(1-E_i) + Q_{ji}\tau_{0j,i}(1-E_j), \quad \tau_{0j,i} = \tau_{0j}/\tau_{0i}.$$

Note that when $d_i/\sqrt{D_{li}t_D} \gg 1$, the derivative of the function $W_{li}(x)$ $(W_{li}''(x_{0i}) = 0)$ is a rather "sharp" function as compared to the exponential function $\exp\{-k_ix/z\}$ (see, Refs. [3–5]). This allows us to calculate integrals in Eq. (10) approximately as

$$\sigma(t_D) \cong \frac{1}{d}\sum_{i=1}^{2} d_i\sigma_{0i}\begin{cases} 1 - \frac{3}{8}\frac{l_{0i}}{d_i - x_{0i}(t_D)}, & k_i \gg 1, \\ \frac{3}{4}\frac{(d_i - x_{0i}(t_D))^2}{d_il_{0i}}\ln\frac{l_{0i}}{d_i - x_{0i}(t_D)}, & k_i \ll 1, \end{cases}$$

where

$$l_{0i} = v_0 \tau_{0i}, \quad x_{0i}\left(t_D\right) = a_{li}\sqrt{D_{li}t_D}, \qquad a_{li} \approx 2\ln^{1/2}\left\{2\sigma_{efi}n_{0i}C_0\sqrt{D_{li}t_D}\right\}. \tag{21}$$

Here, x_{0i} is the effective decrease of the thickness of the ith layer caused by bulk interdiffusion of metals.

Thus, we can find changes of the electrical conductivity of the multilayered films caused by the diffusion annealing

$$\Delta\sigma = \sigma\left(0\right) - \sigma\left(t_D\right) = \frac{1}{d}\sum_{i=1}^{2}\sigma_{0i}x_{0i}\begin{cases}\frac{3}{8k_i}, & k_i \gg 1,\\ \frac{3}{2}k_i\ln\frac{1}{k_i}, & k_i \ll 1.\end{cases}$$

Increasing annealing times we obtain that $\sqrt{D_{li}t_D} \approx d_i$ and the distribution of impurities across the sample becomes almost uniform. Therefore, one may consider the impurity concentration in each layer as a coordinate-independent function which is equal to the average value

$$\overline{C}_{li}\left(t_D\right) = \frac{1}{d_i}\int_0^{d_i} dx C_{li}\left(x, t_D\right), \tag{22}$$

$$\overline{C}_{l1} = C_0\left\{\gamma_l - \left(1-\gamma_l\right)\left[erf\frac{1}{\sqrt{t_{l1}}} - \sqrt{\frac{t_{l1}}{\pi}}\left(1-\exp\left(-\frac{1}{t_{l1}}\right)\right)\right]\right\},$$

$$\overline{C}_{l2} = C_0\gamma_l\left\{erfc\frac{1}{\sqrt{t_{l2}}} + \sqrt{\frac{t_{l2}}{\pi}}\left(1-\exp\left(-\frac{1}{t_{l2}}\right)\right)\right\}.$$

This simplification allows us to calculate integrals in Eq. (10) and to demonstrate that the conductivity of the multilayered film, $\overline{\sigma}\left(t_D\right)$, may be written as

$$\overline{\sigma}\left(t_D\right) = \frac{1}{d}\sum_{i=1}^{2}d_i\sigma_{0i}\overline{\Phi}_i\left(t_D\right), \tag{23}$$

$$\overline{\Phi}_i\left(t_D\right) = \frac{k_i}{\overline{k}_i}\left\{1 - \left\langle\overline{G_i}\left(t_D\right)\right\rangle\right\} \cong \begin{cases}\frac{k_i}{\overline{k}_i}\left(1 - \frac{3}{8\overline{k}_i}\left(1 - P_{ij} - Q_{ji}\overline{\tau}_{j,i}\right)\right), & \overline{k}_i \gg 1,\\ \frac{3}{4}\frac{(1+P_{ij})(1-P_{ji})+Q_{ij}Q_{ji}+2Q_{ji}d_{j,i}}{(1-P_{ij})(1-P_{ji})-Q_{ij}Q_{ji}}k_i\ln\frac{1}{\overline{k}_i}, & \overline{k}_i \ll 1.\end{cases}$$

Here, functions $\overline{G_i}\left(t_D\right)$ given by Eqs. (20) with the following substitution

$$k_i \rightarrow \overline{k_i}\left(t_D\right) = \frac{d_i}{\overline{l_i}\left(t_D\right)}, \qquad E_i \rightarrow \overline{E_i}\left(t_d\right) = \exp\left\{-\frac{\overline{k}_i\left(t_D\right)}{z}\right\},$$

$$\tau_{0j,i} \rightarrow \overline{\tau}_{j,i}\left(t_D\right) = \tau_{0j,i}\frac{1 + l_{0i}\sigma_{efi}n_{0i}\overline{C}_{li}\left(t_D\right)}{1 + l_{0j}\sigma_{efj}n_{0j}\overline{C}_{lj}\left(t_D\right)}, \overline{l_i}\left(t_D\right) = \frac{l_{0i}}{1 + l_{0i}\sigma_{efi}n_{0i}\overline{C}_{li}\left(t_D\right)}. \tag{24}$$

Here, $\overline{l_i}\left(t_D\right)$ is the effective mean-free path in the ith layer after the diffusion annealing.

At large annealing times, when $\sqrt{D_{li}t_D} > d_i$, the dependence of the conductivity σ on the bulk diffusion coefficients D_{li} is rather complicated. In this case, the exact result (10) should be used to describe experimental data. (Note, in calculating impurity concentration we need take into account the presence of the interlayer interfaces, see, e.g. Ref. [17].) The curves shown in Fig. 2a-c were calculated numerically from the exact expression (10). These curves depict the dependence of the conductivity of the multilayered film with a single-crystal structure on the annealing time.

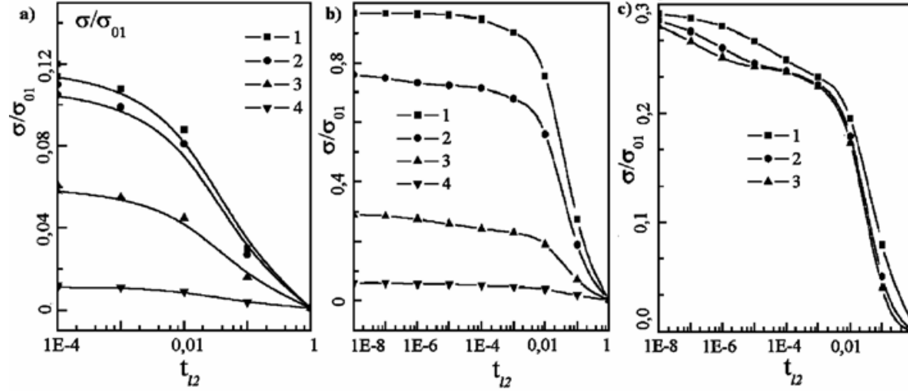

Fig. 2 Calculation of the conductivity (in units of σ_{01}) of a multilayered film consisting of single-crystal layers vs dimensionless annealing time $t_{l2} = (4D_{l2}/d_2^2)\ t_D$. The model parameters are: a) $Q_{ij} = 0.1$, $P_{ij} = 0.2$, $A_i = 1500$, $D_{l2,1} = 0.1$, $k_2 = 0.1$, $l_{2,1} = 0.5$: $1 - d_{1,2} = 0.01$, 2- $d_{1,2} = 0.1$,3-$d_{1,2} = 1$, 4-$d_{1,2} = 10$; b) $Q_{ij} = 0.1$, $P_{ij} = 0.2$, $A_i = 1500$, $D_{l2,1} = 1$, $d_{1,2} = 1$, $l_{2,1} = 1 : 1 - k_2 = 10$, $2 - k_2 = 1$, $3 - k_2 = 0.1$, $4 - k_2 = 0.01$; c) $Q_{ij} = 0.1$, $P_{ij} = 0.2$, $k_2 = 0.1$, $D_{l2,1} = 1$, $d_{1,2} = 1$, $l_{2,1} = 1$: 1-$A_i = 1000$, $2 - A_i = 5000$, $3 - A_i = 10000$.

4 Grain-boundary diffusion in multilayered polycrystalline films

A theoretical analysis of the effect of grain-boundary diffusion on the conductivity of multilayered polycrystalline films (Fig. 1b) may be carried out using modified Mayadas-Shatzkes model [14]. This model takes into account changes in the grain-boundary reflection factor R_{0i} of electrons caused by the migration of the impurity atoms along the grain boundaries in the course of the grain-boundary interdiffusion. This technique was used in Refs. [7–9] to find the dependence of the conductivity of a polycrystalline film on the annealing time. We will follow these works. In spite of the simplicity of the model we obtain some numerical results which are compared with experimental ones.

At sufficiently low temperatures of annealing, when $T < 0.38T_m$ (where T_m is the melting temperature), the mass transfer in polycrystalline films occurs mainly along the grain boundaries [20, 21]. Therefore, during the course of interdiffusion the electrical resistance of the film, caused by the electron scattering at external surfaces and in the bulk of the sample, remains practically unchanged, although the resistance of the grain boundaries is essentially changed by segregation of impurity atoms.

At low concentration of the diffusing impurity atoms at the grain boundaries, $C_{bi}(x,t_D) \ll 1$, the grain-boundary-reflection factor may be written in the following form [7–9].

$$R_i(x,t_D) = R_{0i} + \gamma_{bi} C_{bi}(x,t_D).$$

The characteristic bulk-scattering rate (see Eq. (3)) is given by

$$\frac{1}{\tau_i(x,p_y)} = \frac{1}{\tau_{0i}} \left\{ 1 + \alpha_{0i} \frac{1 + (\gamma_{bi}/R_{0i}) C_{bi}(x,t_D)}{1 - (\gamma_{bi}/(1-R_{0i})) C_{bi}(x,t_D)} \frac{p_0}{|p_y|} \right\}. \tag{25}$$

Here, $R_{0i} = const$ corresponds to the grain-boundary reflection of electrons in the absence of the impurity atoms. The coefficient γ_{bi} is of the order of unity and it has an arbitrary sign because the penetration of impurity atoms into the grain boundaries may both decrease and increase the electron reflection factor R_i. If the grain-boundary-diffusion process is accompanied by forming solid solutions [22], the conductivity of a multilayered film decreases with time, i.e., $\gamma_{bi} > 0$. Along with the scattering at the grain boundaries, electrons may be scattered by elastic-deformation fields in the region near the grain boundaries. The impurity atoms give rise to the relaxation of these fields, and this leads to negative values of γ_{bi} and, therefore, to an increase in the conductivity of the plate [7–9].

If the inequality $\sqrt{D_{li} t_D} \ll \delta_i$, holds ($\delta_i$ is the width of diffusion grain boundary), diffusion of the impurity atoms out of the grain boundaries into the bulk of the sample can be neglected [23] and the diffusion flux can be considered as one-dimensional [24, 25]. Therefore,

$$C_{bi}(x,t_D) = C_{0i} \exp\{-\beta_i x\}, \quad \beta_i = \left\{ \frac{2}{\delta_i D_{bi}} \left(\frac{D_{li}}{\pi t_D} \right)^{1/2} \right\}^{1/2}, \tag{26}$$

where D_{bi}, is the grain-boundary diffusion coefficient in the ith layer, β_i, is the characteristic penetration depth of the impurities into the bulk of metal near a grain boundary.

The conductivity of a multilayered sample with a polycrystalline structure before the diffusion annealing ($t_D = 0$) is determined by Eq. (18), where the thickness-dependent functions $\Phi_{bi}(0)$ are given as

$$\Phi_i(0) = T(\alpha_{0i}) - \langle\langle G_{bi}(0) \rangle\rangle, \tag{27}$$

$$\langle\langle ... \rangle\rangle = \frac{6}{\pi k_i} \int_0^{\frac{\pi}{2}} d\varphi \cos^2\varphi \int_0^1 dz \frac{(z - z^3)(1 - E_{bi})}{H_i^2} \left\{ \; ... \; \right\}, \tag{28}$$

$$E_{bi} = \exp\left\{ -\frac{k_i H_i}{z} \right\}, \quad H_i = 1 + \frac{\alpha_{0i}}{\cos\varphi \sqrt{1-z^2}},$$

and the conductivity of a polycrystalline sample [14]

$$T(\alpha_{0i}) = 1 - \frac{3}{2}\alpha_{0i} + 3\alpha_{0i}^2 - 3\alpha_{0i}^3 \ln\left(1 + \frac{1}{\alpha_{0i}}\right) \cong \begin{cases} 1 - \frac{3}{2}\alpha_{0i} + 3\alpha_{0i}^2, & \alpha_{0i} \ll 1, \\ \frac{3}{4\alpha_{0i}} - \frac{3}{5\alpha_{0i}^2}, & \alpha_{0i} \gg 1. \end{cases}$$

Functions $G_{bi}(0)$ may be obtained from Eq. (20) by the following substituting

$$E_i \to E_{bi}, \quad \tau_{0j,i} \to \tau_{j,i} = \tau_{0j,i}\frac{H_i}{H_j} \equiv \tau_{0j,i}H_{i,j}.$$

In the case when layers of the multilayered film are thick enough, i.e. $d_i \gg l_{0i}$, one can obtain the following asymptotical formulae which are valid for $\alpha_{0i} \ll 1$ and $\alpha_{0i} \gg 1$

$$\Phi_i(0) \cong \begin{cases} 1 - \frac{3}{2}\alpha_{0i} - \frac{3}{8k_i}\left\{(1-P_{ij})\left(1-\frac{32}{3\pi}\alpha_{0i}\right) - Q_{ji}\tau_{0j,i}\left(1-\frac{16}{3\pi}(\alpha_{0i}+\alpha_{0j})\right)\right\}, & \alpha_{0i} \ll 1, \\ \frac{3}{4\alpha_{0i}}\left\{1 - \frac{1}{4k_i\alpha_{0i}}\left[(1-P_{ij})\left(1-\frac{512}{105\pi\alpha_{0i}}\right) - Q_{ji}\tau_{0j,i}\frac{\alpha_{0i}}{\alpha_{0j}}\left(1-\frac{256(\alpha_{0i}+\alpha_{0j})}{105\pi\alpha_{0i}\alpha_{0j}}\right)\right]\right\}, & \alpha_{0i} \gg 1. \end{cases} \tag{29}$$

In the case when the thickness of the layer, d_i, is much smaller than the electron mean-free path l_{0i}, i.e. $k_i \ll 1$, we obtain the following approximated expressions of the functions $\Phi_{bi}(0)$

$$\Phi_{bi}(0) = \frac{3}{4}\frac{(1+P_{ij})(1-P_{ji}) + Q_{ij}Q_{ji} + 2Q_{ji}d_{j,i}}{(1-P_{ij})(1-P_{ji}) - Q_{ij}Q_{ji}}k_i \begin{cases} \ln\frac{1}{k_i}, & \alpha_{0i} \le k_i, \\ \ln\frac{1}{k_i} - \frac{4}{\pi}\alpha_{0i}, & k_i < \alpha_{0i} \ll 1, \\ \ln\frac{1}{\alpha_{0i}k_i}, & 1 < \alpha_{0i} \ll \frac{1}{k_i}. \end{cases} \tag{30}$$

Consequently, after the diffusion annealing $t_D \neq 0$, the conductivity of the multilayered polycrystalline film is given by Eq. (10) where the thickness-depending functions $\Phi_i(t_D)$ are given by

$$\Phi_i(t_D) = \frac{1}{2}k_i^2\left\langle\left\langle\frac{G_{bi}(t_D)H_i^2}{z^2(1-E_{bi})}\right\rangle\right\rangle. \tag{31}$$

Calculating functions $G_{bi}(t_D)$ (see Eqs. (12-14)) we have to make the following substitution $W_{li}(x) \to W_{bi}(x)$, where

$$W_{bi}(x) = \exp\left\{-\frac{k_i(H_i-1)}{z}\left[1 - x + \frac{\sqrt[4]{t_{bi}}}{R_{0i}}\ln\left(\frac{1-R_{0i}-\gamma_{bi}C_{0i}\exp\left(-(t_{bi})^{-1/4}\right)}{1-R_{0i}-\gamma_{bi}C_{0i}\exp\left(-x(t_{bi})^{-1/4}\right)}\right)\right]\right\}, \tag{32}$$

$$t_{bi} = \frac{\pi\delta_i^2 D_{bi}^2}{4d_i^4 D_{li}}t_D \tag{33}$$

Note, $W_{bi}(x)$ gives the probability that electrons travel the distance $[x, 1]$ without scattering at the grain boundaries (those are channels of the impurity migration).

At small diffusion times, $\beta_i^{-1} \ll d_i$, we can calculate Eq. (10) approximately. Thus, we obtain the following formulas for the conductivity of a multilayered film consisting of the thick metal layers ($d_i \gg l_{0i}$)

$$\sigma(t_D) \cong \frac{1}{d}\sum_{i=1}^{2} d_i\sigma_{0i}\begin{cases} 1-\frac{3}{2}\alpha_{0i}\left(1+\frac{1}{R_{0i}\beta_i d_i}\ln\left[1+\gamma_{bi}C_{0i}\frac{1-\exp(-\beta_i d_i)}{1-(R_{0i}+\gamma_{bi}C_{0i})}\right]\right), & \alpha_{0i}\ll 1,\\ \frac{3}{4\alpha_{0i}}\left(1+\frac{1}{(1-R_{0i})\beta_i d_i}\ln\left(1-\gamma_{bi}C_{0i}\frac{1-\exp(-\beta_i d_i)}{R_{0i}+\gamma_{bi}C_{0i}}\right)\right), & \alpha_{0i}\gg 1.\end{cases} \tag{34}$$

Consequently, we can calculate changes of the conductivity due to the annealing, $\Delta\sigma = \sigma(0) - \sigma(t_D)$, in the case of thick polycrystalline layers ($k_i \to \infty$)

$$\Delta\sigma = \frac{1}{d}\sum_{i=1}^{2}\sigma_{0i}\beta_i^{-1}\begin{cases} \frac{3}{2}\alpha_{0i}\left[R_{0i}\left(\frac{1-R_{0i}}{\gamma_{bi}C_{0i}}-1\right)\right]^{-1}, & \alpha_{0i}\ll 1,\\ \frac{3}{4\alpha_{0i}}\left[(1-R_{0i})\left(1+\frac{R_{0i}}{\gamma_{bi}C_{0i}}\right)\right]^{-1}, & \alpha_{0i}\gg 1.\end{cases} \tag{35}$$

At large diffusion annealing times, $\beta_i^{-1} < d_i$, we may use the aforementioned approximation of the average concentration (22). The impurity distribution along the grain boundaries is supposed to be uniform and it may be written as

$$\overline{C}_{bi}(t_D) = C_{0i}\sqrt[4]{t_{bi}}\left\{1-\exp\left(-\frac{1}{\sqrt[4]{t_{bi}}}\right)\right\}. \tag{36}$$

Here, t_{bi} is given by Eq. (33). This assumption allows us to perform the integration over x in (13 – 14) and obtain the conductivity of the multilayered polycrystalline film in the form (23) where functions $\overline{\Phi}_i(t_D)$ can be found from equations (27 – 29) with the following substitutions

$$\Phi_i(0) \to \overline{\Phi}_i(t_D), \quad T(\alpha_{0i}) \to \overline{T}(\overline{\alpha}_{0i})$$

$$\alpha_{0i} \to \overline{\alpha}_i(t_D) = \alpha_{0i}\frac{1+(\gamma_{bi}/R_{0i})\overline{C}_{bi}(t_D)}{1-(\gamma_{bi}/(1-R_{0i}))\overline{C}_{bi}(t_D)}. \tag{37}$$

At an arbitrary ratio between the values β_i^{-1} and d_i the experimental data may be analyzed numerically using Eq. (10). Fig. 3 a-c depicts the dependence of the conductivity of multilayered film with polycrystalline structure on the annealing time calculated numerically for different values of the parameters under the conditions of the grain-boundary interdiffusion.

5 Conclusion

In summary, metal interdiffusion essentially influences the conductivity of multilayered single-crystal and polycrystalline metal films. At small diffusion-annealing times, t_D, the characteristic penetration depth of the impurities (which is of the order of $\sqrt{D_{li}t_D}$ for a single-crystal film and $\left\{(2/(D_{bi}\delta_i))(D_{li}/\pi t_D)^{1/2}\right\}^{-1/2}$ for a polycrystalline film) is much smaller than the layer thickness, d_i, and size effects are determined by the thickness of a "pure" region of the layer. Thus, using experimental data on changes of the conductivity due to the diffusion annealing, one can estimate the depths of penetration of the impurities both into the bulk of the layers and into the grain boundaries. Consequently, it allows

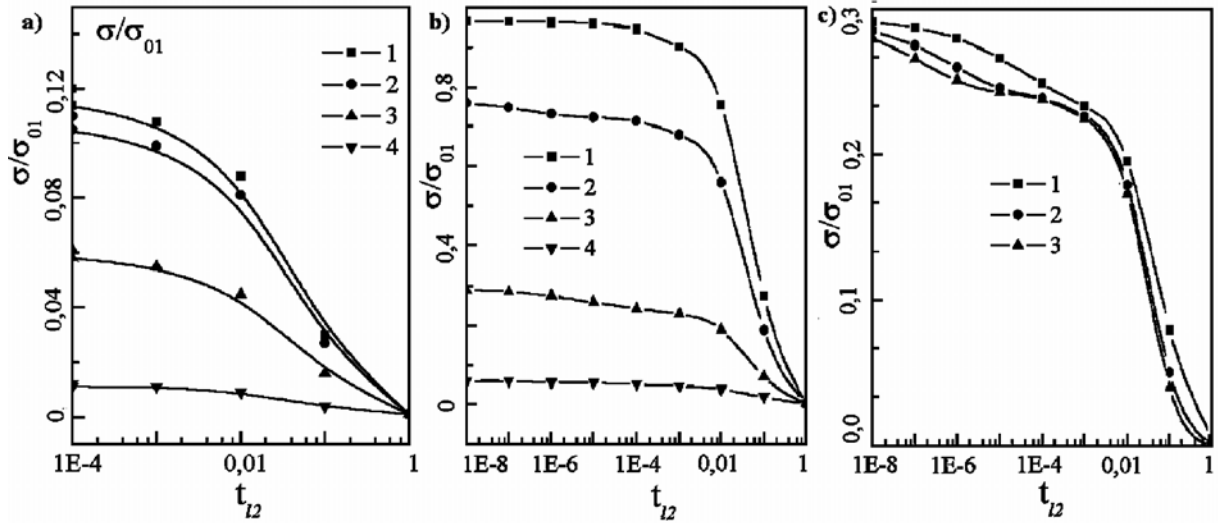

Fig. 3 Conductivity of a multilayered polycrystalline film (in units of σ_{01}) versus dimensionless annealing time $t_{b2} = \frac{\pi \delta_2^2 D_{b2}^2}{4 d_2^4 D_{l2}} t_D$. The model parameters are: a) $Q_{ij} = 0.1$, $P_{ij} = 0.2$, $D_{l2,1} = 0.1$, $d_{1,2} = 0.1, l_{2,1} = 0.5$, $C_{0i} = 0.1, \alpha_i = 3$, $R_{0i} = 0.5$: 1- $k_2 = 10, \gamma_i = -0.5$, 2- $k_2 = 10, \gamma_i = 0.5$,3-$k_2 = 1, \gamma_i = -0.5$, 4- $k_2 = 1, \gamma_i = 0.5$, 5-$k_2 = 0.1, \gamma_i = -0.5$,6- $k_2 = 0.1, \gamma_i = 0.5$; b) $Q_{ij} = 0.1$, $P_{ij} = 0.2$, $D_{l1,2} = 0.1$, $k_2 = 0.1$, $l_{2,1} = 0.5$, $C_{0i} = 0.1, \alpha_i = 5$, $R_{0i} = 0.5$: 1-$d_{1,2} = 50$, 2- 3- $d_{1,2} = 5$, 4- $d_{1,2} = 1$, 5-$d_{1,2} = 0.1$; c) $Q_{ij} = 0.1$, $P_{ij} = 0.2$, $D_{l2,1} = 0.1$, $d_{1,2} = 0.1, l_{2,1} = 0.5$, $C_{0i} = 0.1, \alpha_i = 3$, $k_2 = 0.1, R_{0i} = 0.5$: 1-$\gamma_{bi} = -1$, 2- $\gamma_{bi} = -0.5$,3-$\gamma_{bi} = 0.0$, 4-$\gamma_{bi} = 0.5$, 5-$\gamma_{bi} = 1.0$.

for estimating the coefficients of bulk and grain-boundary diffusion. At large diffusion-annealing times, the characteristic penetration depth of the impurities is of the order of the layer thickness. To analyze changes of the conductivity in this case, one may use the aforementioned approximation of the average concentration. We obtain the relation between the values of conductivity of a multilayered film, the effective electron mean-free path after the diffusion annealing and the averaged grain-boundary diffusion coefficients (see Eq. (35)). This creates the possibility to estimate the coefficients of the impurity diffusion.

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