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GRAIN-BOUNDARY DIFFUSION IN Cu AND Ni FILMS WITH THIN METAL COATING

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Investigation results of the grain-boundary diffusion in Cu films with thin Ni coating and in Ni films with thin Cu coating by the low-temperature resistometric method are presented in this work. It is shown that during the coating deposition and thermal annealing the irreversible increase in the electrical resistance by the value from tenth parts to a few Ohms is observed. This is caused by the diffusion processes of coating atoms on the grain boundaries of base layers.

Keywords: *GRAIN-BOUNDARY DIFFUSION, DIFFUSION PROCESSES, GRAIN BOUNDARY, THIN COATING, AVERAGE GRAIN SIZE.*

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1. INTRODUCTION

Diffusion processes, which have significant influence on the electrophysical properties of thin metal films, lead to the changes in the microscopic parameters describing the charge carrier scattering on the external and internal boundaries and in the grain volume [1].

In world publications a great attention is paid to the study of diffusion processes in polycrystalline and nanocrystalline materials (see, for example, [2-14]). Authors of Ref. [4] generalized investigation results of the diffusion processes in film systems and bulk samples.

Grain boundary (GB) is the transition region with the width up to 3 nm, for which the lattice of one grain with certain crystallographic orientation is transformed into the lattice of another grain, which has another crystallographic orientation. Therefore the higher energy state of electrons and the distorted crystal structure are observed on GB. As a result, such structure is an easier way for atom diffusion than the grain volume. Activation energy of the diffusion process along GB is substantially less than of the bulk diffusion, and so the atom transfer occurs faster by two orders of magnitude than in the volume of the perfect crystal [2].

At first sight it seems that the grain-boundary diffusion of foreign atoms only leads to the more chaotic structure of the grains, and as a result the transmission coefficient decreases. But based on the analysis within the framework of the thermodynamic approach [15] we conclude that the defect healing process on GB by coating atoms can also takes place, and this will cause the increase in the GB transmission coefficient for conduction electrons. Conclusions of [15] are proved by the results of [14], where investigation of the electrophysical properties of two-layer Cu/Cr films in conditions of mutual diffusion was performed.

In [16] the results of theoretical investigations of the transport size effects in two-layer polycrystalline films were systematized depending on the width of the system components. It is concluded that at small coating thickness with respect to the base film ($d_c/d << 1$, where d is the thickness of the base film, d_c is the coating thickness) its own contribution to the kinetic coefficients means little, but its absolute value differs from the value for the single-layer film because of the possibility of charge carrier scattering not only on the external surface, but also on the interface of metal layers. Presence of impurities in the grains leads to the changes in their scattering properties, and can both increase (in the case when diffusion process leads to the solid solution formation) [16] and decrease (if diffusant atoms stimulate the relaxation of elastic fields nearby the grain boundaries) [17] the electron scattering coefficient by the grain boundaries. Diffusion annealing of polycrystalline sample can lead both to the increase in the conduction and to its decrease [16] that is agreed with conclusions of the above-cited publications.

Note, that the authors of the cited papers used the secondary ion mass spectrometry (SIMS) or the Auger electron spectroscopy (AES) methods for the diffusion study. Another method for determination of the diffusion coefficients was proposed in [5] and used in [6]. Thus, the authors of [5] while investigating the influence of diffusion processes on the electrical resistance in two-layer film systems based on Ag and Au showed, that in the grain-boundary diffusion process the film resistance conditioned by the phonon and surface scattering is not changed. Resistance change on the grain boundaries is caused by the appearance of electric charges there, by the change in intermolecular forces and vibrational spectrum and due to the formation of new phases on the grain boundaries. Moreover, penetration of diffusant atoms into GB can condition both the resistance increase and its decrease [5].

Analysis of the publications [18-20] shows that the coating deposition on the film surface changes its electrophysical properties, in particular, due to the grain-boundary diffusion of foreign atoms from the coating. This can lead both to the improvement and deterioration of the grain boundary transparency in consequence of the defect healing or formation of new defects on GB. Since the grain-boundary diffusion influences the electrophysical properties we have carried out its investigation using the low-temperature resistometric method, which was proposed in [5] and was used later in [6].

2. EXPERIMENTAL TECHNIQUE AND THE RESULTS PROCESSING

Low-temperature resistometric method is based on the determination of the electric resistance change due to the diffusion during the annealing process. Known [5], that at the relatively low temperatures T_{an} of diffusion annealing ($T_{an} < 0{,}3T_m$, where T_m is the melting temperature) the bulk diffusion is almost stopped, and mass transfer in metals is realized along the GB only that leads to the changes in their properties. Therefore studying the electrophysical properties of film materials (in particular, the electrical resistance), in accordance with [5] it is possible to find important information about the parameters of the grain-boundary diffusion. The grain-boundary diffusion coefficient D is determined using the data of precision measurements of the electrical resistance during diffusion annealing.

During the grain-boundary diffusion the electrical resistance of the film conditioned by the phonon and surface scattering remains unchanged. But

the GB resistance can be changed due to the appearance of electric charges nearby the boundaries, the changes in intermolecular forces and vibrational spectrum, the defect healing or formation of new defects, and due to the formation of new phases on the boundaries. Also assumed [21], that nearby grain boundaries the elastic fields are spread at the distance of the order of boundary structure period. Electron scattering occurs both on the boundary itself and on the deformation field. Penetrating into the boundary, diffusant atoms stimulate the relaxation of the deformation fields. Then the electron scattering, and the total film resistance as well, will be changed. Therefore according to [21], penetration of diffusant atoms into GB can cause both the increase and decrease in the electrical resistance R of the film.

For monoblock in thickness films during the annealing at $T_{an} < 0{,}3T_m$ and in the case of infinite solubility of diffusant atoms in the film, absence of diffusion over the sample surface and the interphases, the concentration profile of the diffusant in the film, in accordance with [5], can be described by the following expression:

$$c(x,\tau) = c_0\left[\frac{d_n}{l} + \sum_{n=1}^{\infty}\frac{2}{n\pi}\sin\frac{n\pi a}{l}\cos\frac{n\pi x}{l}\left(-\frac{n^2\pi^2 D\tau}{l^2}\right)\right], \quad (1)$$

where d_n is the thickness of diffusant layer; $l = d + d_n$ is the total thickness of the film and diffusant layer; c_0 is the atom concentration of diffusing component in the time moment $\tau = 0$; τ is the time of diffusion annealing.

Using correlation (1) it is impossible [5] to calculate the change in the electrical resistance of the sample during diffusion annealing for any time moment τ. Firstly, dependence of the resistance R on c for the whole range of diffusant concentrations is unknown. Secondly, theory of electron scattering by the grain boundaries, which would take into account the change in R over the film thickness, is absent. However, for the case $a/l \leq 0{,}1$ the value of $D\tau/l^2$ (starting from it the electrical resistance is not changed) can be estimated. It follows from (1) that at $D\tau/l^2 \geq 0{,}1$ the concentration profile of the diffusant, and so the electrical resistance, is not almost changed. Therefore, the time moment τ^* when the change in R ceases can be found from expression

$$D\tau^*/l^2 \cong 0{,}1, \quad (2)$$

where τ^* is the time of resistance measurement, which is conditioned by the grain-boundary diffusion.

The grain-boundary diffusion coefficient can be obtained from (2). Experimental realization of the given method is described in [5, 6]. We used expression (2) for determination of the low-temperature grain-boundary diffusion coefficient. The value of l was calculated as the sum of the thickness of Cu (Ni) base layer and the effective thickness of Ni (Cu) coating up to 2 nm. τ^* is considered to be the time from the beginning of the relatively sharp growth of the electrical resistance up to its linear increase or saturation.

During investigation of the diffusion processes of Cu and Ni films with thin metal coating by the resistance method the following sequence of the experiment was realized:

1-st stage: to obtain by the thermal method the film samples of Cu and Ni base film with certain geometric configuration at temperatures of polycor

substrate, which are close to the Debye temperature for the bulk samples; then to cool them to room temperature (the deposition rate for Cu and Ni films was 1,5-2,5 and 0,4-0,8 nm/s, respectively).

2-nd stage: annealing (without vacuum failure) of the base films in accordance with the scheme "heating ↔ cooling" during 2-3 cycles in the temperature range of 300-550 K (Cu) and 300-630 K (Ni) for thermal stabilization of the electrophysical properties and healing of the crystal structure defects.

3-d stage: deposition (without vacuum failure) of the thin metal coating ($d_c \sim 2$ nm) by the thermal method with subsequent system stabilization during 30 min and fixation of the resistance change after coating deposition at the temperature $T = 300$ K.

4-th stage: diffusion annealing of the system at $T = 373$ K during 30 min.

5-th stage: diffusion annealing of the system at $T = 473$ K during 30 min.

6-th stage: diffusion annealing of the system at $T = 533$ K during 30 min.

Note, the choice of temperatures for diffusion annealing was conditioned by the resistometric method requirements, since, according to [10], only if $T_{an} < 0,3T_m$ the diffusion along GB will take place.

Annealing temperature was fixed by the copper-constantan thermocouple, which had the direct contact with the substrate, using the voltameter M2051 (accuracy is ± 1 K). Thickness of the base films was determined by the interferometric method using the device MII-4. At thickness > 40-50 nm the measurement accuracy was ~ 10-20%. Effective thickness of the metal coating was determined from the sample mass and by the quartz resonator method, which allowed to find the coating thickness with the accuracy to 10%.

Investigation of the phase and structural composition of film samples was performed by the methods of transmission electron microscopy and electron diffraction (device PEM-125K), and investigation of the surface topology was carried out by the atomic force microscopy (AFM). For the electron-microscopic and the electron-diffraction study the polycrystalline films were condensed on the carbon films-substrates, and in the case of the surface topology study the dielectric glass-ceramic plates were used.

Cu and Ni films (Fig. 1a,b) have the fcc-structure with the interplanar distances and lattice parameters (a) close to those, which the bulk samples have (a_0): Cu − $a = 0,3612$ nm ($a_0 = 0,3615$ nm [22]), Ni − $a = 0,3528$ nm ($a_0 = 0,3524$ nm [22]). Cu and Ni coatings with effective thickness up to 5 nm have the isle structure, and their phase composition corresponds to the phase composition of continuous films with the fcc-lattice, though the lattice parameter has a larger value in comparison with the bulk samples and single-layer films: $a_{Cu} = 0,3625$ nm, $a_{Ni} = 0,3534$ nm. Annealed Cu and Ni films with Ni and Cu coatings, respectively, also have the fcc-lattice with the lattice parameters close to those for single-layer films.

Fig. 2 gives an idea about the average grain size (L) in Cu and Ni base films subject to the thickness. Analysis of this data shows, that in the case of Cu films one can assert about the larger value of the average grain size in comparison with the thickness. Thus, in the thickness range $d = 20\text{-}70$ nm L changes from 40 to 110 nm. The average grain size in Ni films (Fig. 2) has values of the order of the film thickness. This coincides with the results obtained by other authors (see, for example, [23-25]).

Results of the surface topological investigation of Cu film samples with thin Ni coating in the unannealed and the annealed states are presented in Fig. 3. Under annealing of Ni(2)/Cu(35)/Sub films up to the temperature T_{an} = 550 K the increase in the surface roughness is observed that is connected with the diffusion processes of Ni atoms into Cu base film.

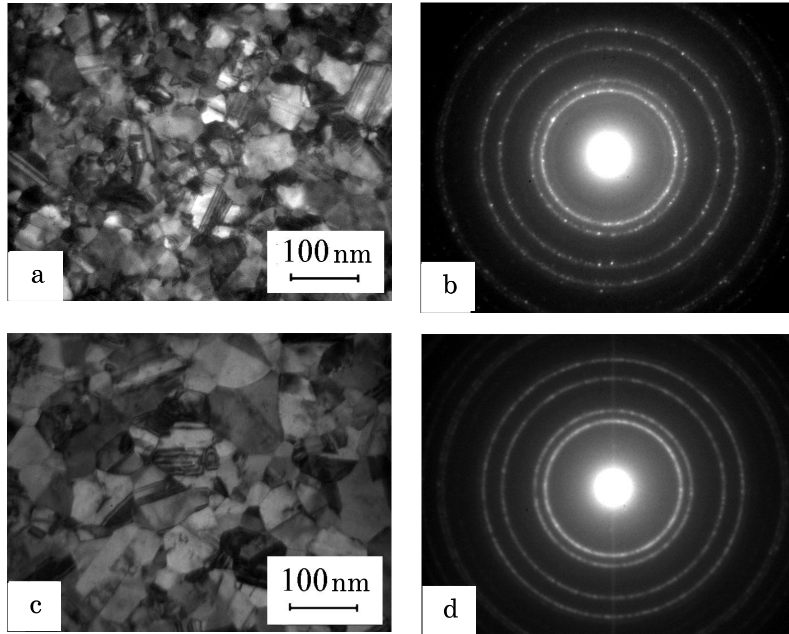

Fig. 1 *– Crystal structure and the electron-diffraction patterns from Cu(42) (a, b) and Ni(52) (c, d) films after thermal treatment. Film thickness in nm is given in round brackets*

Deposition of Ni coating with the effective thickness of $d_c \sim 2$ nm on the surface of Cu base film smoothes it in a certain way at the level of 1-2 nm. But after thermal treatment Ni atoms diffuse into Cu base film. As in the previous case, this leads to the increase in the surface roughness decreasing its reflectivity and returning it to the initial state that is confirmed by the investigation results both of the structural and phase composition and of the diffusion processes by the SIMS method [26].

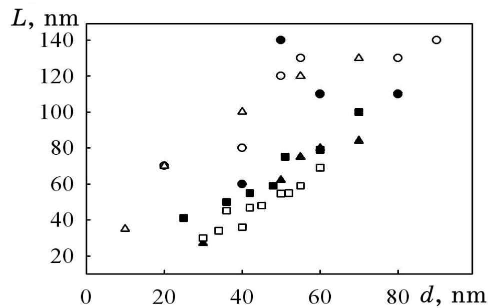

Fig. 2 *– Dependence of the average grain size L on the film thickness d for Cu films: ■ – our results; ● – data of the paper [23]; ○ – data of the paper [24]; Δ – data of the paper [25]; for Ni films: □ – our data; ▲ – data of the paper [23]*

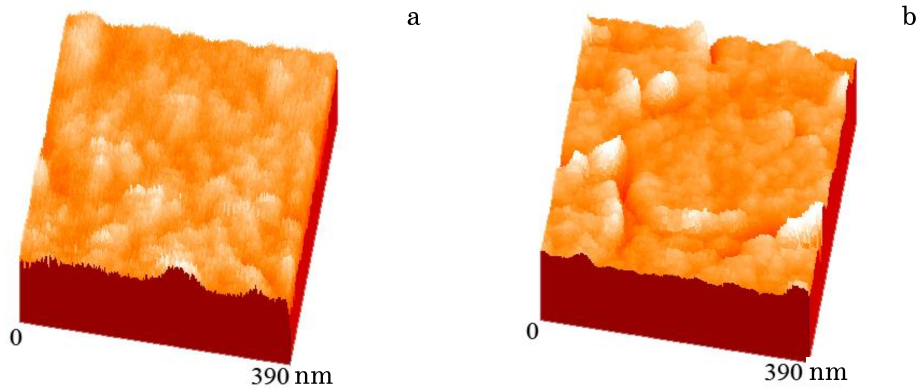

***Fig. 3** – AFM picture in the regime of the surface profile of the unannealed (a) and the annealed (b) up to T_{an} = 550 K Ni(2)/Cu(35)/Sub film samples*

3. INVESTIGATION OF THE GRAIN-BOUNDARY DIFFUSION PROCESSES

Typical dependences of the resistance on the diffusion annealing time for Cu films of the relatively small thickness with thin coating (d_c ~ 2 nm) are shown in Fig. 4. As seen from Fig. 4a, the coating deposition does not lead to perceptible changes in the resistance. Under annealing at the temperature of 373 K (Fig. 4b) at first the electrical resistance decrease from 9,5 to 9 Ohm is observed, and this decrease takes place during 1 min.

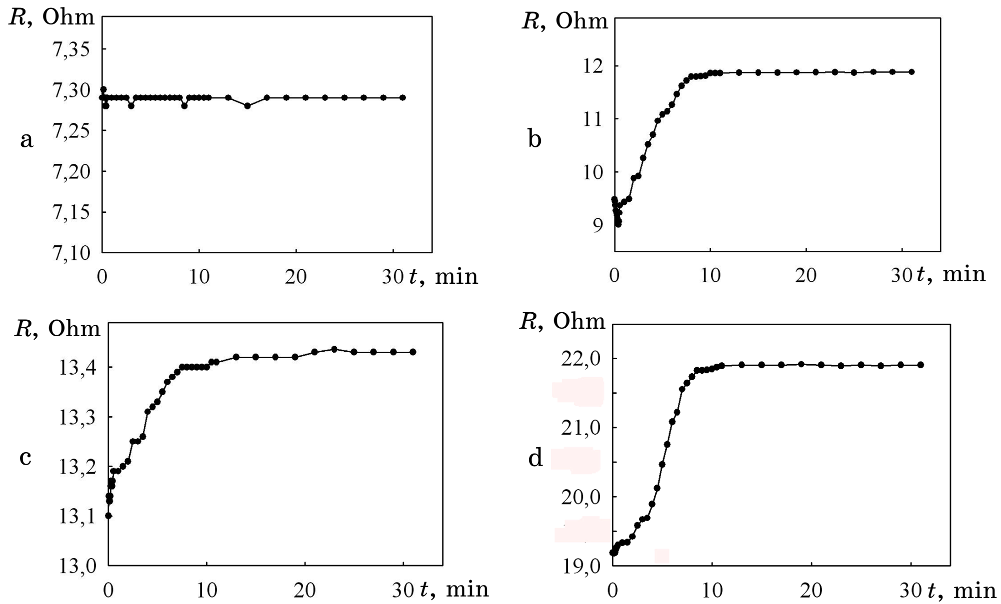

***Fig. 4** – Dependence of the resistance on the annealing time for Ni/Cu(40)/Sub system at the temperatures of 300, 373, 473 and 533 K (a-d, respectively)*

It would be reasonable to suggest that the resistance decrease can be caused by healing of excess defects in Cu films, but further investigation shows the fallacy of this assumption, since such decrease in Cu/Sub film system is observed even after three cycles of thermal treatment and additional film stabilization at the temperature of 373 K during 30 min (see Fig. 5). It may be connected with insufficient temperature for defect healing. Thus, the resistance decrease at the initial stages of the exposure at T_{an} = 373 K is typical both for Cu films without coating and Ni/Cu/Sub film systems. So, this is not caused by the Ni coating atom diffusion into the volume of Cu film.

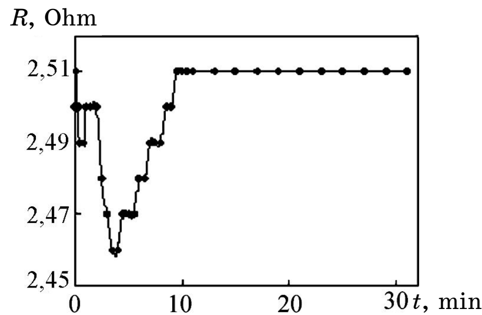

***Fig. 5** – Dependence of the resistance on the annealing time for Cu film (d = 52 nm) at the temperature of 373 K*

After the specified change in the resistance its pronounced increase is observed that can be connected with the grain-boundary diffusion. Diffusion time is the time interval between the completion of resistance drop and its attainment of saturation. Comparing data for Cu films with coating and uncoated films, which are presented in Fig. 4 and 5, we can note the following. In Cu films after minimum the resistance increases to the value, which approximately corresponds to the resistance before exposure. In Ni/Cu/Sub film systems the resistance increases by some Ohms.

We also performed the experiments when Ni coating was deposited at T_{an} = 373 K and thermal stabilization was realized during 30 min at the same temperature (Fig. 6a). In this case we observed the initial decrease in the resistance by the value of the order of 0,05 Ohm, and then the resistance increase by 0,10 Ohm. Such small total change in the resistance can be connected with the diffusion taken place during the condensation of Ni coating layer on Cu base layer. The next step was the annealing of this film at T_{an} = 473 K (Fig. 6b).

If compare data for thicker Cu films with Ni coating and results for Ni/Cu/Sub films of smaller thickness, we can note that in the samples of greater thickness the initial decrease in the resistance is not fixed. The value of ΔR, the resistance increases by, is equal to 0,1 Ohm in comparison with some Ohms for relatively thin samples. Such a result can be caused by two factors. Firstly, the resistance of the thicker samples has smaller value in comparison with thin samples; therefore the resistance change will be smaller. Secondly, the greater thickness of Cu film, the greater its average grain size is. Increase in the average grain size causes the weakening of the grain-boundary diffusion [6], since films with greater average grain size have smaller total area of grain boundaries. We should note, that the authors of [27] observed the same change in the resistance. In particular, the largest value of ΔR was fixed in the case when Cr base film had relatively small thickness at the thickness of Ge coating of about 2,8 nm. Increase in the base

film thickness leaded to the sharp decrease in the value of resistance change for the coated films.

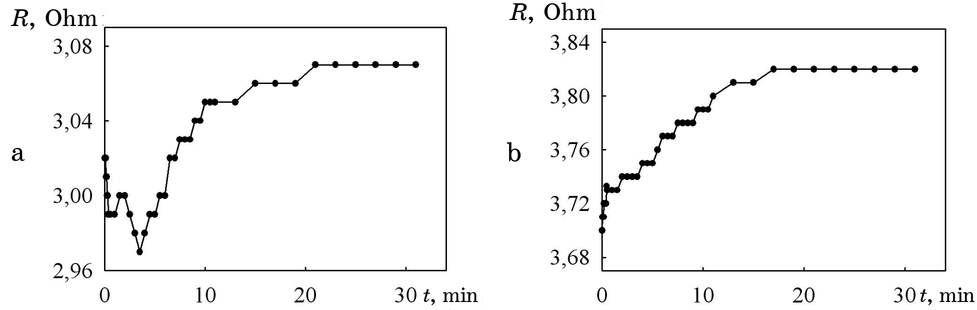

Fig. 6 *– Dependence of the resistance on the annealing time for Ni/Cu(*51*)/Sub film system under the coating deposition at* T_c = 373 *K and annealing at the same temperature (a) and under the thermal stabilization at* T_{an} = 473 *K (b)*

Consider results of the same investigation for Ni films with Cu coating. Typical dependences of the electrical resistance on the time of diffusion annealing are presented in Fig. 7. These dependences correspond to the same ones for Ni/Cu/Sub film system (see, for example, Fig. 4) except for the resistance decrease at the temperature of 300 K (that is after coating deposition) and the initial decrease in the resistance under annealing at T = 373 K. Under exposure at T = 373 K the sharp increase in the resistance occurs by the value of some Ohms, and after that its attainment of saturation takes place during τ^* = 18 min.

The resistance change at the temperatures of 473 and 533 K occurs in the same way, but the resistance decreases only by 0,5-0,8 Ohm. The time τ^* when the resistance increases is also less than in the case of exposure at the temperature of 373 K.

If compare the electrical resistance of the films with the freshly-deposited coating and the electrical resistance of the films after exposure at T = 533 K and cooled to room temperature, we can note that in the case of Cu films with Ni coating the resistance increases on average by 100%, and for Ni films with Cu coating – by 65%.

The main reason for increase in the electrical resistance in coated films is connected with the change in the conditions of electron scattering on the grain boundaries in the base films due to the diffusion of other atoms. Calculation of the parameters of the charge transfer was performed in [28-29]. In accordance with this data in Cu (Ni) films the deposition of thin Ni (Cu) coating leads to the increase (decrease) in the coefficient R of the charge carrier scattering on the grain boundaries (in the coefficient r of the charge carrier transmission through the grain boundaries) due to the formation of additional scattering defects on the boundaries. Thus, for example, the values of r and R were the following: 0,38 and 0,51 (Ni/Cu/Sub, T = 360 K) and 0,94 and 0,05 (Cu/Ni/Sub, T = 300 K) in comparison with 0,41 and 0,46 (Cu/Sub, T = 360 K) and 0,97 and 0,02 (Ni/Sub, T = 300 K), respectively. $|\Delta r/r|$ for Ni/Cu/Sub films was 7,3% and 2,6% for Cu/Ni/Sub films in comparison with the base uncoated films [28-29].

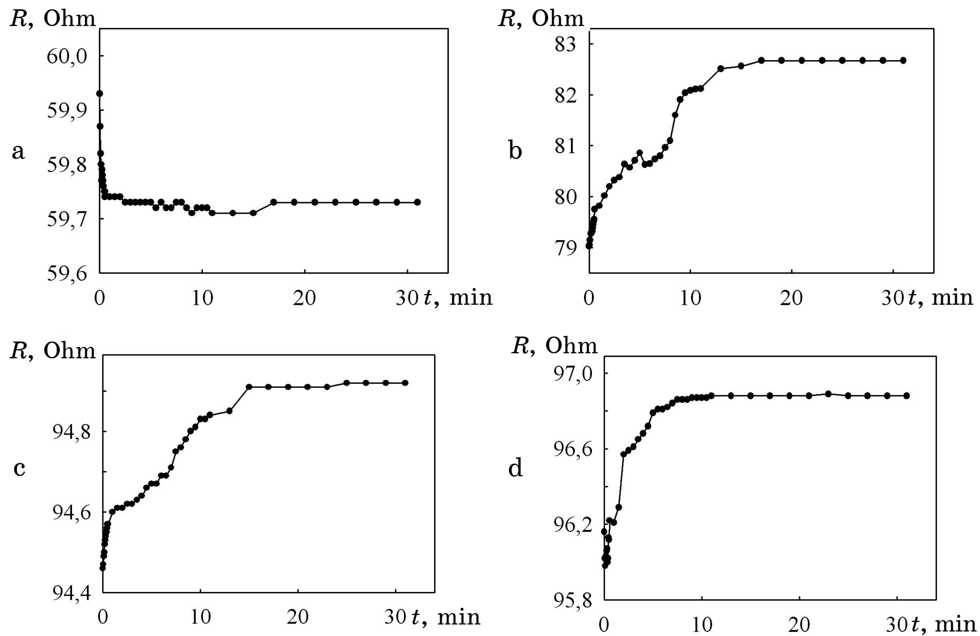

Fig. 7 – *Dependence of the resistance on the annealing time for Cu/Ni(*60*)/Sub system at the temperatures of* 300, 373, 473, 533 *K (a-d, respectively)*

Calculation of the grain-boundary diffusion coefficients for film systems with coating was performed using (2), and the results of these calculations are presented in Table 1.

Table 1 – *Grain-boundary diffusion coefficients*

Film system	d, nm/L, nm	$D \cdot 10^{19}$, m^2/s		
		T_{an} = 373 K	T_{an} = 473 K	T_{an} = 533 K
Ni/Cu/Sub	36/50	5,2	5,1	5,1
	40/53	5,0	4,7	4,6
	42/55	4,7	4,6	–
	45/60	4,6	4,6	4,5
	53/72	4,2	4,1	–
	60/79	4,1	4,0	4,0
	71/100	3,8	3,7	3,5
Cu/Ni/Sub	32/32	5,1	5,0	–
	40/36	4,8	4,5	4,4
	51/55	4,6	–	–
	60/69	4,5	4,3	4,1

As follows from Table 1, the increase in the average grain size of base film causes the decrease in the grain-boundary diffusion coefficient. Such a result corresponds to the conclusions of [1, 18-20] and other publications, since the decrease in the average grain size leads to the increase in the diffusion coefficient due to the increase in the total area of grain boundaries.

Determined values of the grain-boundary diffusion coefficients coincide in the order of magnitude with those obtained by the SIMS method [26] and with known data (for example, [1, 9-12, 18-20, 30, 31]), where calculation of D was performed both by the SIMS and AES methods.

4. CONCLUSIONS

The main conclusions of the present paper are summarized as follows:
1. Under exposure of coated film samples for half an hour at the temperatures of 373, 473 and 533 K the irreversible increase in the electrical resistance during 6-20 min by the value from tenth parts to a few Ohms is observed that is caused by the grain-boundary diffusion processes of coating atoms.
2. With the increase in the average grain size the decrease in the grain-boundary diffusion coefficient occurs in base layers, since the decrease in the average grain size leads to the increase in the diffusion coefficient due to the increase in the total area of grain boundaries.

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