J. Nano- Electron. Phys.
1 (2009) No2, P. 79-89

PACS numbers: 66.30.Pa, 68.35.Fx, 72.10.Fk

DIFFUSION PROCESSES AND INTERFACE ELECTRON SCATTERING IN FILM SYSTEMS BASED ON Cu/Fe AND Fe/Cr

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Investigation results of diffusion processes by the SIMS and the AES methods in Cu/Fe and Fe/Cr film systems are represented; influence of the annealing temperature on the effective thermal diffusion coefficients is studied. Values of the interface transmission coefficient and the effective diffusion coefficients in different processes, namely, the condensation-stimulate diffusion, the ion-stimulate one, and the thermal diffusion, are calculated.

Keywords: *DIFFUSION PROFILE, SIMS, DIFFUSION COEFFICIENT, INTERFACE ROUGHNESS, INTERFACE TRANSMISSION COEFFICIENT.*

(Received 8 September 2009, in final form 2 October 2009)

1. INTRODUCTION

Discovery of the giant magnetoresistance phenomenon observed in low-dimensional heterogeneous magnetic film materials (multilayers and granular alloys) constantly stimulates the investigations of different processes, including diffusion and structural phase transformations. In spite of the great research efforts a number of questions is still little studied. In particular, investigation of the diffusion processes along the grain boundaries or across the interface. As it was shown in [1] the grain-boundary diffusion in polycrystalline film systems, in contrast to bulk samples, in the most cases dominates over the bulk one differing by two orders.

Among the number of investigated multilayer structures the film systems based on Fe/Cu and Fe/Cr fragments are of permanent interest due to their wide application in modern electronics [2, 3]. These film systems are representatives of two opposite tendencies from the point of view of the atom interdiffusion: extremely low mutual solubility of Fe and Cu atoms or infinite solubility in the case of Fe and Cr atoms [4].

A lot of publications (see, for example, [5-8]) are devoted to the study of structural and phase state of the interfaces in multilayer structures and their influence on the value of magnetoresistance (MR) as well. The authors of [5] by the Mossbauer spectroscopy method showed that the interface region between Fe and Cu layers represents an alloy and its relative fraction in Fe layer growths with decrease of layer thickness of Fe(x)/Cu(x) system from $x = 3$ nm to $x = 1$ nm. Analysis of the influence of the interface roughness on the Fe and Cr layer boundary on the value of MR of multilayer film systems on their basis was carried out in [6, 7]. In particular, it was proposed to take into account the influence of the interdiffusion of differenttype atoms across the interfaces, which leads to change of the exchange interaction due to the fraction decay with antiferromagnetic ordering. It was established, that with the growth of the interface roughness the MR gradually decreases [7].

The aim of the present investigation consisted in study of the atom interdiffusion during the condensation of film systems and their thermal treatment, in calculation of the interdiffusion coefficients and determination of the interface scattering parameters in multilayer structures based on Fe/Cu and Fe/Cr fragments subject to the interconnection of the pointed processes with the structural phase state of film systems.

2. EXPERIMENTAL TECHNIQUE

Thin-film two- and multilayer systems based on Fe and Cu or Cr were obtained by the thermal evaporation method in the vacuum (the pressure of the remaining atmosphere was 10^{-3}-10^{-4} Pa) on the amorphous glass-ceramic (for the SIMS investigation) or crystalline Si(111) (for the X-ray analysis) substrates (Sub). The thickness control of some layers was realized in situ by the quartz resonator method.

To study the thermoresistive properties of three-layer film systems the glass-ceramic substrate with contact pads of the stage form was used. Heat setting of the film was carried out in the temperature interval from the room temperature to 700 K (in the case of Cu/Fe/Cu system) and to 950 K (for Cr/Fe/Cr system).

Investigations of the diffusion processes in two-layer film systems were realized by the secondary-ion mass spectrometry (SIMS) method using the device MS-7201M. To obtain the diffusion profiles we have carried out the recording of the secondary ion mass-spectrums versus the thickness, while ion etching of the sample was performed by Ar^+ with energies in the range from 5 to 50 keV. Concentration c_0 was determined by the averaged signal of secondary ions from the bulk standard plates of Cu, Fe, and Cr.

The interface quality was studied by the X-ray reflectometry method using the device X'Pert MRD Pro with copper Kα radiation.

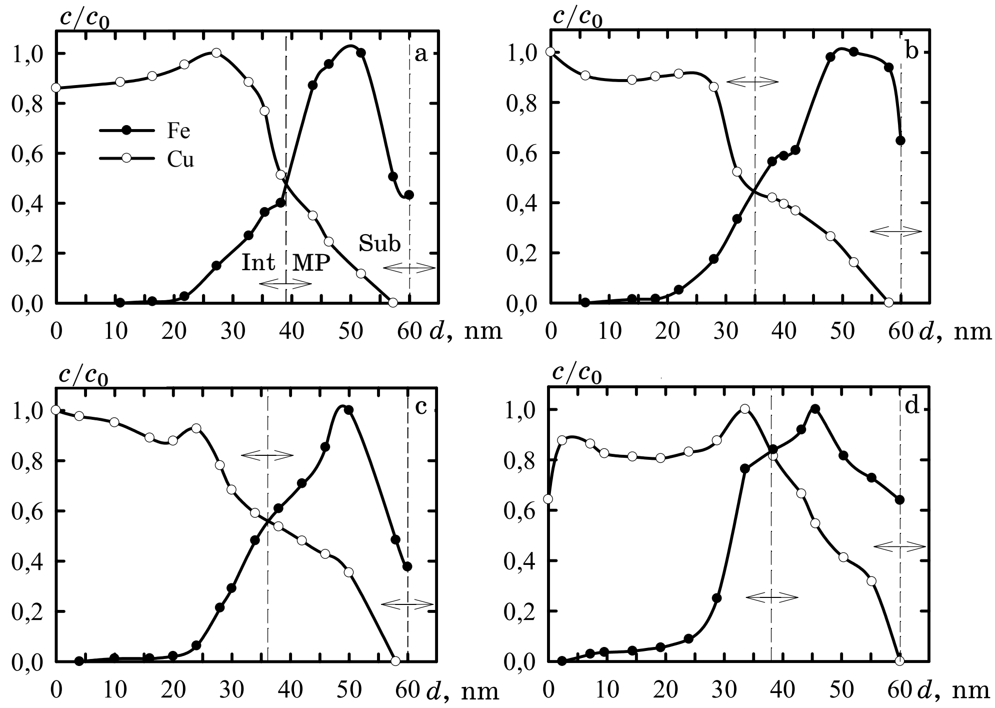
3. EXPERIMENTAL RESULTS

3.1 Diffusion processes

Investigations of the diffusion processes in Cu/Fe/Sub and Fe/Cr/Sub film systems were carried out by the SIMS method during the alternate primary ion etching of the unannealed samples (the condensation-stimulate diffusion (CSD)) and the annealed ones to different temperatures in the range from 300 to 900 K (the thermal diffusion (ThD)).

In observable systems the diffusion profiles, as a result of the CSD realization (Fig. 1, 2), have different nature in the unannealed samples: their partial overlapping in the case of Cu/Fe system (Fig. 1a) and complete mixing of atoms in Fe/Cr system (Fig. 2a). Diffusion profiles obtained from the annealed samples undergo changes, which consist either in their further overlapping (Fig. 1b-e) in the case of Cu/Fe system or in appearance of the blurred interface (Int) coinciding with Matano plane (MP) and broad peaks on diffusion profiles (Fig. 2b-d) in the case of Fe/Cr system. Here, the interface displacement is observed that is completely explained within the

Kirkendall effect [9]. Such form and transformation difference of diffusion profiles is directly connected with the structural phase state of investigated samples. Thus, in samples of Cu/Fe system the individuality of some layers is mostly remained up to the temperature 750 K, while in Fe/Cr system the solid solution (Fe, Cr) [4] is already formed during the condensation and its ordering is partly occurred under the thermal annealing that appears in diffusive stratification of the solution or in the so-called effect of a vacancy flux reversal, which was observed earlier in [10].



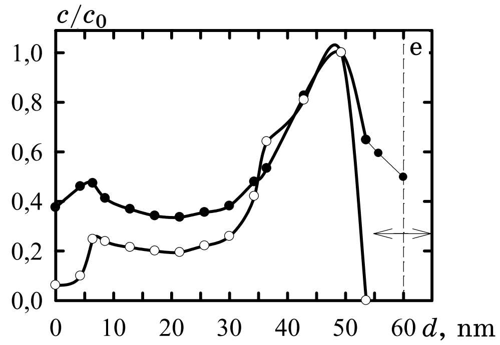


***Fig. 1** – Diffusion profiles for Cu(40)/Fe(20)/Sub film system in the unannealed (a) and the annealed to* T_{ann} = 500 *K (b),* 630 *K (c),* 750 *K (d),* 870 *K (e) states*

We note, such component stratification was observed by the authors of [11] while kinetics of the diffusion processes in Ag/Cu system with limited mutual solubility of the components was investigated. As shown in [12], under thermal treatment of two-layer Fe/Cr system saturation or supersaturation of a solid solution can occur at a surplus of one of the components. This solution was created during the CSD as the result of the atom extraction, segregated on the interfaces, into the grain volume.

We have to point out, that the ion-stimulate diffusion (ISD), the contribution of which into the total diffusion cannot be taken into account, has a certain effect on a shape of diffusion profiles while using the SIMS technique.

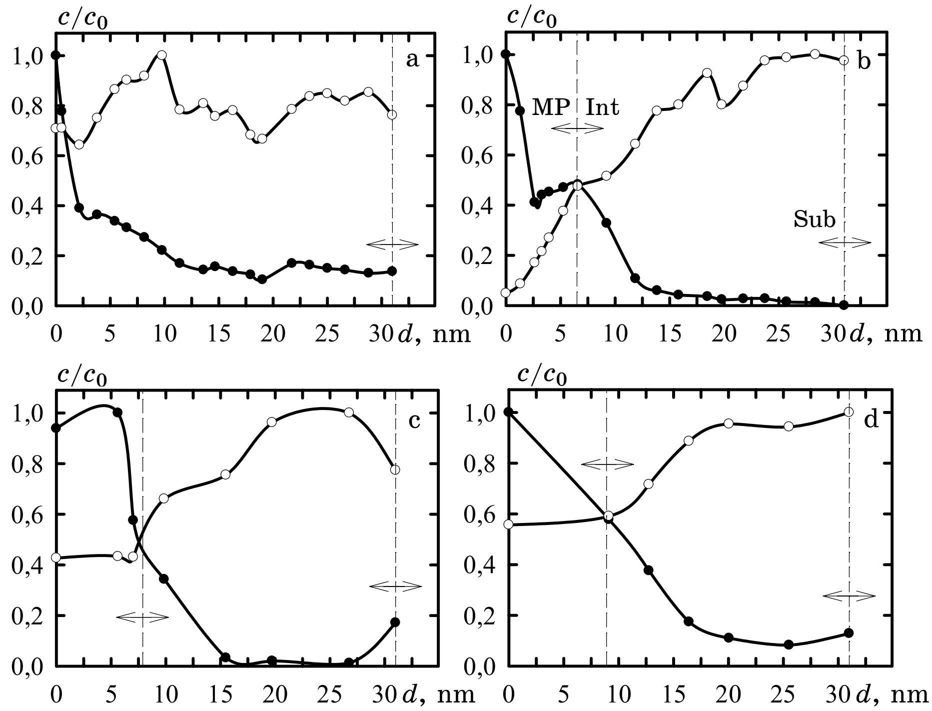


***Fig. 2** – Diffusion profiles for Fe(10)/Cr(21)/Sub film system in the unannealed (a) and the annealed to T_{ann} = 600 K (b), 750 K (c), 900 K (d) states*

Considering the above mentioned remark and based on the obtained data (Fig. 1, 2), the effective coefficients of the CSD and ISD (D_1), of the CSD, ISD and ThD (D_2), and of the ThD (D_{ThD}) were calculated using the following relations:

$$l_c \cong (D_1 \tau_c)^{1/2}, \quad (1)$$

$$l_{th} \cong (D_2 \tau_{th})^{1/2}, \quad (2)$$

$$l_{th} - l_c \cong (D_{\mathrm{ThD}} \tau_{th})^{1/2}, \quad (3)$$

where l_c and l_{th} are the diffusion path lengths of atoms for the cases of the CSD + ISD and the ThD, respectively (they were determined as the thickness of upper layer, at which the Auger-signal from lower-layer atoms vanishes, or as the thickness of scoured lower layer, at which the signal from upper-layer atoms on the SIMS-spectrum vanishes); τ_c and τ_{th} are the condensation and the thermal annealing times, respectively.

We note, that the diffusion profile subtraction allowed to calculate D_{ThD} in pure form using relation (3) (as in the case of the Auger-electron spectroscopy (AES)), that is impossible to do in two other cases mentioned above. Calculation results are represented in Table 1.

Table 1 *– Effective diffusion coefficients of atoms in film systems based on Fe and Cr or Fe and Cu*

Diffusion couple	CSD (AES) [13, 14]		ThD (T_{ann} = 673 K) (AES) [13]		CSD + ISD (SIMS)		CSD + ISD + ThD (SIMS)							
	l, nm	$D\cdot10^{19}$, m^2/sec	Δl*), nm	$D\cdot10^{19}$, m^2/sec	l, nm	$D\cdot10^{19}$, m^2/sec	l, nm	$D\cdot10^{19}$, m^2/sec	l, nm	$D\cdot10^{19}$, m^2/sec	l, nm	$D\cdot10^{19}$, m^2/sec	l, nm	$D\cdot10^{19}$, m^2/sec
Cr → Fe	Fe(10)/Cr(10)/Sub [1]				Fe(10)/Cr(21)/Sub									
							T_{ann} = 450 K		T_{ann} = 600 K		T_{ann} = 750 K		T_{ann} = 900 K	
	3,0	0,50	2,0	0,004	10,0	4,4	10,0	4,5	10,0	3,6	10,0	3,3	10,0	1,1
Fe → Cr	Cr(5)/ Fe(10)/Sub [1]													
	2,5	0,90	1,0	0,020	21,0	19,6	21,0	20,0	21,0	16,2	21,0	14,7	21,0	4,7
Cu → Fe	Fe(10)/Cu(10)/Sub				Cu(40)/Fe(20)/Sub									
							ThD (SIMS)							
							T_{ann} = 500 K		T_{ann} = 630 K		T_{ann} = 750 K		T_{ann} = 870 K	
							Δl, nm	$D\cdot10^{19}$, m^2/sec	Δl, nm	$D\cdot10^{19}$, m^2/sec	Δl, nm	$D\cdot10^{19}$, m^2/sec	Δl, nm	$D\cdot10^{19}$, m^2/sec
	2,2	0,30	–	–	17,3	87,7	0,7	0,02	0,7	0,01	2,7	0,11	3,7	0,14
Fe → Cu	Cu(10)/Fe(10)/Sub													
	3,0	0,25	–	–	29,1	248,9	4,9	0,72	6,9	0,97	8,5	1,06	10,9	1,21

*) $\Delta l = l_{th} - l_c$

Dependences $D_{\mathrm{ThD}}(T)$ in ($\ln D_{\mathrm{ThD}}$, $1/RT$) coordinates allow to calculate the activation energy of diffusion and the preexponential factor D_0 in diffusion equation. Obtained data for Fe/Cu system can be written in the form of diffusion equations:

$$D_{\mathrm{Cu\to Fe}}(T) = 3,3\cdot10^{-19}\cdot\exp(-\frac{24150}{RT}),\ D_{\mathrm{Fe\to Cu}}(T) = 2,4\cdot10^{-19}\cdot\exp(-\frac{4980}{RT}),$$

where the activation energy of diffusion is given in J/mol.

Calculations showed that D_1 is two orders more than D_{ThD} that is explained by the saturation of grain boundaries by another atoms during the condensation of the upper layer. Here, the CSD for Cu/Fe system is one order more than for Fe/Cr system (see Table 1). These differences can be explained based on the structural phase state data of investigated samples. Obtained differences of diffusion coefficients in the unannealed samples are connected with more intensive grain-boundary diffusion during the condensation in comparatively coarse-grained Cu/Fe system in contrast to Fe/Cr system, where both the grain-boundary and the bulk diffusions take place simultaneously.

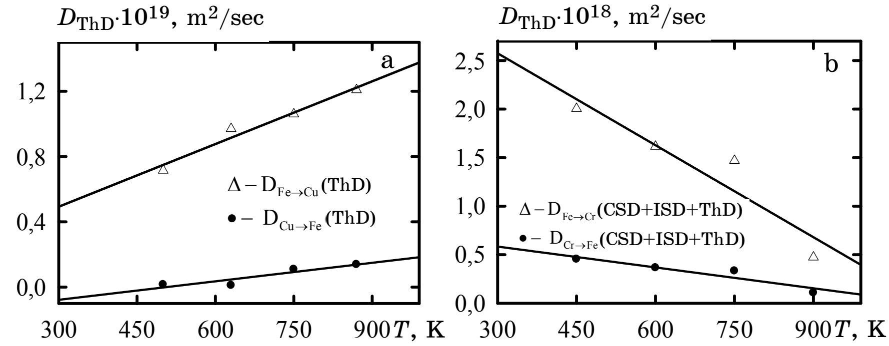


***Fig. 3** – Dependence of the effective coefficient of the thermal diffusion versus the annealing temperature for film systems: Cu(40)/Fe(20)/Sub (T_{ann} = 500 K, 630 K, 750 K and 900 K) (a) and Fe(10)/Cr(21)/Sub (T_{ann} = 450 K, 600 K, 750 K and 900 K) (b). Calculation of D_{ThD} was realized using relations (2) (a) and (3) (b)*

3.2 Interface properties and the interface transmission coefficient

Based on the data of [15] it is possible to conclude that the best interface quality (with minimal roughness) can be achieved in systems, components of which have infinite mutual solubility (for example, Fe/Cr, Fe/V and others). In [16] it was shown by the example of Fe/Cr and Fe/Cu systems that the interface roughness is much less for the first system in comparison with the second one. Abovementioned conclusions about the interface structural state for the unannealed and the annealed samples are somewhat confirmed by the X-ray reflectometry data. It shows, that in the unannealed state the interface quality ($\sigma_{Fe/Cr}$ = 0,2 nm and $\sigma_{Cr/Fe}$ = 1,2 nm) in Fe/Cr system is much better than in Fe/Cu one ($\sigma_{Fe/Cu}$ = 1,2 nm and $\sigma_{Cu/Fe}$ = 1,4 nm). And the interface roughness essentially increases after the thermal treatment (for example, $\sigma_{Fe/Cr}$ = 1,4 nm and $\sigma_{Cr/Fe}$ = 2 nm) (Fig. 4). Calculation data for the thickness and the roughness of individual layers in multilayer systems based on Fe/Cr in the unannealed and the annealed states is represented in Table 2.

As seen from this data the roughness $\sigma_{nm/m}$ of the nonmagnetic/magnetic interface dominates over the $\sigma_{m/nm}$ that correlates with the value of diffusion coefficients.

Ref. [17] is one of the first publications where the study technique of the interface electron scattering in Au/X/Au (X = Fe, Co, and Ni) three-layer polycrystalline films is proposed. Theoretical model for the thermal resistance coefficient of two-layer Dimmich films for the limiting case (when the X layer thickness tends to zero) was the analysis basis. Described earlier in

[18] technique allows to estimate the total value of the coefficients of specular reflection and interface transmission, and the influence of grain-boundary scattering as well. In investigated samples we measured the conductivity of two series of three-layer Cu/Fe/Cu and Cr/Fe/Cr film systems at different thickness of the intermediate Fe layer. In this case the thickness of Cu and Cr film was constant and equal 20 nm. In Fig. 5 we show the schematic representation of film system at the fixed (a) and the "vanishing" (b) thickness of intermediate layer.

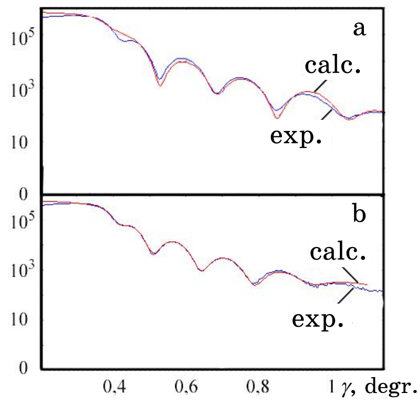


Fig. 4 *– X-ray reflectometry dependencies for [Cr(5)/Fe(5)]$_2$/Si(111) film system in the unannealed (a) and the annealed to 700 K states (b)*

Table 2 *– Calculation results of the thickness and the roughness of individual layers for [Cr(5)/Fe(5)]$_2$/Si(111) film system*

Unannealed			Annealed to 700 K		
layer	d, nm	σ, nm	layer	d, nm	σ, nm
1 Sub(Si)	–	1,10	1 Sub(Si)	–	1,10
2 Fe	4,8	0,21	2 Fe	5,4	1,42
3 Cr	5,9	1,14	3 Cr	5,6	2,10
4 Fe	4,9	0,16	4 Fe	5,9	1,37
5 Cr	6,9	1,37	5 Cr	6,1	1,87

For the limiting case, when the intermediate layer thickness tends to zero, relation for the Cu resistivity will take the form:

$$\frac{\sigma}{\sigma_\infty} \cong 1 - \frac{3}{16k}\left(2 - p - Q\right), \qquad (4)$$

where σ is the system conductivity obtained by extrapolation to zero of the σ dependence versus the intermediate layer thickness; $k = d/\lambda_\infty$ is the reduced thickness (the average free path λ_∞ and the conductivity $\sigma_\infty = \lim_{d\to\infty}\sigma$ correspond to the bulk condensates). Expression for the sum of coefficients of specular reflection (p) and interface transmission (Q) follows from (4)

$$p + Q = 2 - \frac{16 \cdot d}{3 \cdot \lambda_\infty}(1 - \sigma \times \rho_\infty)\,. \qquad (5)$$

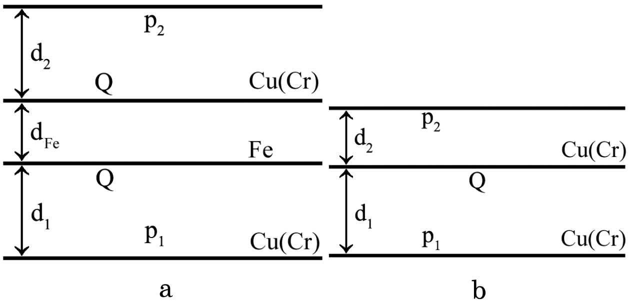


Fig. 5 *– Schematic representation of three-layer film at the fixed (a) and the "vanishing" (b) thickness of the intermediate layer. Q is the interface transmission coefficient; $p = p_1 = p_2$ is the specular reflection coefficient of the film surfaces*

For more correct calculations the author of [17] proposed to use in (5) instead of the ρ_∞ the reduced grain-boundary resistance ρ_g, the value of which can be determined from relation for the Fuchs model in the case $k >> 1$:

$$\frac{\rho}{\rho_\infty} = 1 + \frac{3\lambda_0(1-p)}{8d},$$

i.e., expression for ρ_g can be presented in the form: $\rho_g = \rho_\infty + A/d$, where $A = 3\rho_\infty\lambda_0(1 - p)/8$ is the peculiar constant for each film material; d is the Cu or Cr film thickness.

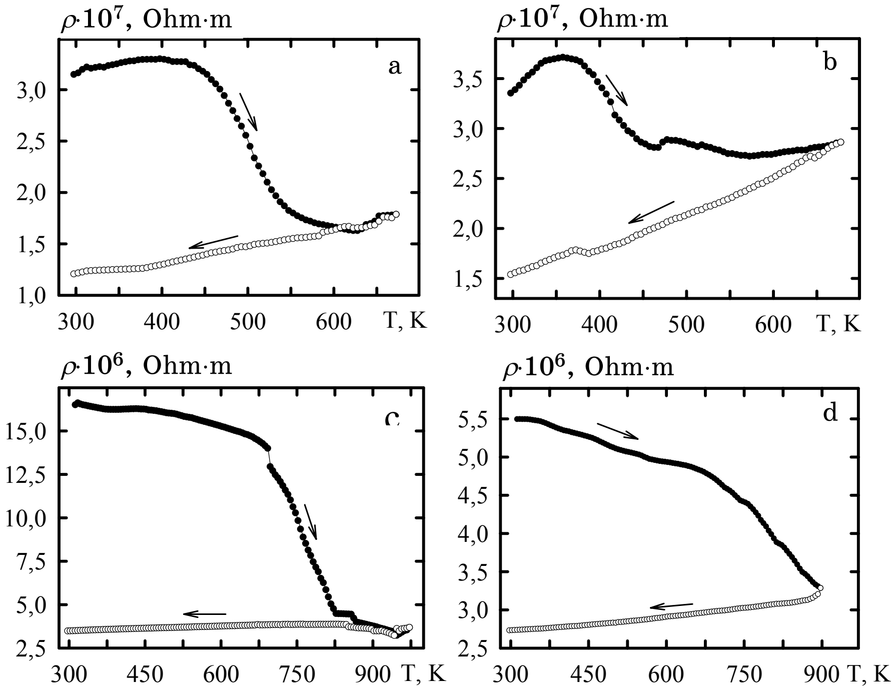


Fig. 6 *– Temperature dependences of the resistivity for film systems: Cu(20)/Fe(d_{Fe})/Cu(20)/Sub (a, b) and Cr(20)/Fe(d_{Fe})/Cr(20)/Sub (c, d). d_{Fe} thickness, nm:* 6,1 *(a),* 12,3 *(b),* 6,5 *(c),* 16 *(d)*

Based on the experimental data for three-layer film systems Cu(20)/ Fe(d_{Fe})/Cu(20)/Sub (Fig. 6a,b) and Cr(20)/Fe(d_{Fe})/Cr(20)/Sub (Fig. 6c,d) we have plotted dependences of the conductivity versus the thickness of Fe layer (Fig. 7). Their approximation to zero allows to define the system conduction at the "vanishing" intermediate layer.

Different nature of the dependences $\sigma(d_{Fe})$ can be explained by different asymptotic values of ρ_∞ for Cu, Fe, and Cr films on the dimensional dependences of ρ versus the intermediate layer thickness.

Relations between the coefficients p and Q for the cases of Fuchs and Mayadas approximations are represented in Fig. 8; and it follows from this figure that in the first approximation $p + Q = 0{,}8$ (Fe/Cu) and 0,6 (Fe/Cr) or $p + Q = 1{,}2$ (Fe/Cu) and 0,7 (Fe/Cr). If take the most typical value of the specular reflection coefficient $p \cong 0{,}2$ it is possible to estimate the interface transmission coefficient: $Q \cong 0{,}4$ (Fe/Cr) - 0,6 (Fe/Cu) for the Fuchs approximation and $Q \cong 0{,}5$ (Fe/Cr) - 1,0 (Fe/Cu) for the Mayadas one, and this is qualitatively agreed with the typical value of the interface transmission coefficient.

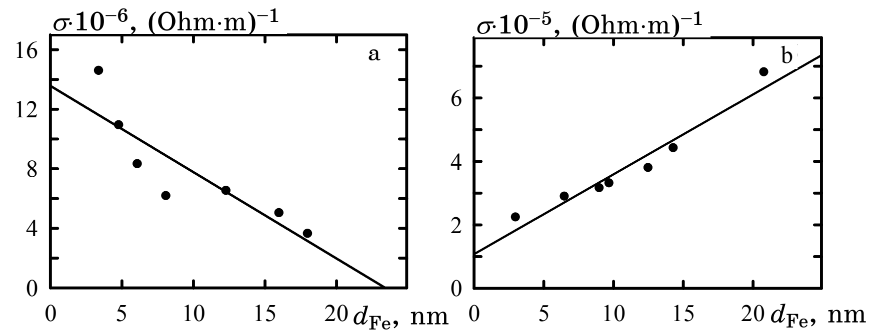


Fig. 7 *– Dependences of the conductivity versus the thickness of Fe intermediate layer for the film systems: Cu(20)/Fe(d_{Fe})/Cu(20)/Sub (a) and Cr(20)/Fe(d_{Fe})/Cr(20)/Sub (b)*

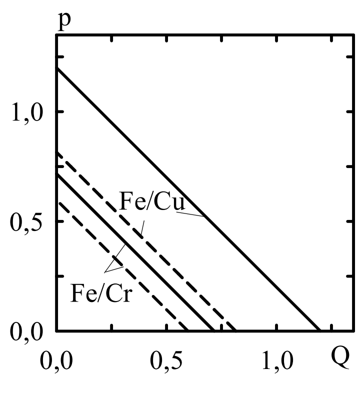


Fig. 8 *– Dependence ($p + Q$) for the Mayadas (solid lines) and the Fuchs (dotted lines) approximations*

4. CONCLUSIONS

Based on the obtained experimental results we can conclude:
1. Processes of atom interdiffusion in Cu/Fe and Fe/Cr film systems have the following peculiarities:

– partial (Cu/Fe) or complete (Fe/Cr) mixing of atoms as the result of the CSD takes place in the unannealed samples;

– under thermal treatment of these film systems the mixing rate of atoms in Cu/Fe system increases, while in Fe/Cr system the partial stratification of the solid solution (Fe, Cr) is observed, that is appeared in blurred maximums on diffusion profiles and their displacement toward the substrate or system surface;

– calculation and comparison of the effective interdiffusion coefficients obtained by the SIMS and the AES methods are carried out; and equations of the thermal diffusion of Cu and Fe atoms are derived.

2. Investigation by the X-ray reflectometry method showed that the roughness $\sigma_{nm/m}$ of the nonmagnetic/magnetic interface dominates over the $\sigma_{m/nm}$ value (for example, $\sigma_{Cu/Fe}$ = 1,4 nm, $\sigma_{Fe/Cu}$ = 1,2 nm; $\sigma_{Cr/Fe}$ = 1,2 nm, $\sigma_{Fe/Cr}$ = 0,2 nm); and this result is agreed with the values of the diffusion coefficients.

3. Based on the de Vries technique the total value of $p + Q$ is calculated in the Fuchs and the Mayadas approximations and the interface transmission coefficient is estimated.

The present work was performed within the financial support of the Ministry of Education and Science of Ukraine (Grant No. 0109U001387).

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