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The Electrical Conductivity of the Three-layer Polycrystalline Co / Ag(Cu) / Fe Films under the Conditions of Atomic Interdiffusion

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The paper presents the results of experimental studies of the crystal structure and electrical resistivity in three-layer Co / Ag / Fe and Co / Cu / Fe nanocrystalline films. It has been shown that all the samples annealed at 700 K with $d_{\mathrm{Cu,Ag}} > 5$ nm are three-phase (FCC-Co, FCC-Ag or FCC-Cu, BCC-Fe). Dependence of the three-layer film resistivity on the layer thickness has been obtained experimentally. It has been detected that the above-mentioned dependence is nonmonotonic that is conditioned by the diffuse nature of the interaction of electrons with conductor interfaces.

Keywords: Crystal structure, Phase composition, Interdiffusion, Diffusion profile, Resistivity, Thermal coefficient of resistance, Interface.

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1. INTRODUCTION

In recent years, a more profound knowledge of thin film physics takes place mainly in studies of the physical properties of multilayer film systems, whose components are both magnetic and nonmagnetic layers with crystal structure varying within an extremely wide range from amorphous to nano- and microcrystal ones. A great attention to the study of the transport phenomena in multilayer film systems is conditioned by both their wide application as an element base in microelectronics and computer science and possibility to obtain an important from the fundamental point of view information about the interaction of conduction electrons with external and interlayer boundaries of multilayer sample. On the other hand, combining metal layers with different transport characteristics, one can obtain a macroscopic sample with principally new physical properties, whose realization is impossible in uniform conductors [1, 2].

Investigations of the transport size effects in two-, three-, and multilayer film systems are analyzed in detail in the literature (see [3-5]), and it is concluded that stability of the transport characteristics of multilayer metal films (electrical conduction, strain sensitivity factor, thermal coefficient of resistance) is connected with diffusion processes accompanied by the phase formation. Fitting of the thermal treatment mode, thickness of separate layers of film materials, concentration of metal components, if phase composition is known, allows to form film systems of a certain structural-phase state with rather stable electrophysical properties.

The aim of the present work consists in the experimental investigation of the dependence of the electrical resistivity and thermal coefficient of resistance (TCR) of polycrystalline three-layer Co / Ag(Cu) / Fe / S films (S is the glass substrate) on the thickness of Ag (Cu) sublayer (under the condition that thicknesses of the base (Fe) and covering (Co) layers are constant) and temperature, and also the features of the behavior of diffusion processes during condensation and annealing.

2. EXPERIMENTAL TECHNIQUE

Film samples were obtained by the method of resistive (Ag, Cu) and electron-beam (Co, Fe) evaporation in the vacuum of 10^{-4} Pa at the substrate temperature of $T_s = 300$ K. Glass polished plates with pre-deposited electric contacts (copper with chromium sublayer) were applied as the substrates in the investigation of electrical conduction of the films. Condensation rate of metal layers was equal to 0.5-0.7 for Co, Fe and 1-1.5 nm/s for Ag, Cu, respectively. Universal digital voltmeter V7-46/1 was used for the determination of the value of electrical resistance R with the relative error of 0.025 %.

Thickness of separate layers d_m was determined by the interferometer method (microinterferometer MII-4 with miniature laser as a light source and computerized interference pattern recording system) with measurement accuracy to 10% at $d > 50$ nm (d is the total thickness of the three-layer film). Stainless steel masks were used to provide the reproduction of film geometry (length a and width b). The value of resistivity was calculated by the correlation $\rho = Rbda^{-1}$.

Ultrathin nonmagnetic sublayers (Ag, Cu) were obtained by the substrate exposure in a vapor steam during 1-10 s using films-witnesses. Condensation process of films-witnesses was equal to 100-150 s that allowed to measure their thickness with the accuracy of 5-10 %. Taking into account the measurement error of the condensation time t_c, calculation error of the effective thickness is 55-60 % at $t_c = 1$ s and decreases to 10-15 % with the increase in t_c to 10 s.

For thermal stabilization of the samples we have used their repeated heating by the following scheme: "heating – exposure at maximum temperature during 30 min – cooling". Heating (cooling) rate was constant and equal to 2-3 K/min in the temperature range of 100-700 K. Temperature was controlled by the chromel-alumel thermocouple with the error of ± 5 K.

Condensates on carbon substrates (electron diffractometer and transmission electron microscope PEM-125K) were applied to investigate the phase composition and film structure.

Diffusion processes in the condensates on glass substrates were investigated by the method of secondary-ion mass-spectrometry (SIMS) using the secondary-ion mass-spectrometer MS-7201M.

3. EXPERIMENTAL RESULTS

Electrical resistivity ρ of freshly condensed at room temperature three-layer Co / Ag / Fe and Co / Cu / Fe films takes the value from $10\cdot10^{-7}$ to $30\cdot10^{-7}$ Ohm·m (depending on the layer thickness). This exceeds (more than by the order of magnitude) the value of ρ_0 for pure metals in a bulk state (for Co $\rho_0 = 6.24\cdot10^{-8}$ Ohm·m, for Cu $\rho_0 = 1.5\cdot10^{-8}$ Ohm·m, for Fe $\rho_0 = 9.71\cdot10^{-8}$ Ohm·m) [6]. Obviously, such value of the resistivity for unannealed films, primarily, is conditioned by the defect structure of freshly condensed layers and fine dispersity of the crystallites [7, 8].

For stabilization of the electrical properties and recrystallization, films were thermally treated during several annealing cycles in the temperature range of 100-700 K. We have to note that for Co / Cu(Ag) / Fe samples with d_N = 5-50 nm (d_N is the thickness of nonmagnetic layer), which underwent a thermal treatment at 700 K, three-phase fcc-Co + bcc-Fe + fcc-Cu (Fig. 1b) and fcc-Co + bcc-Fe + fcc-Ag (Fig. 2b) compositions, respectively, are registered on the electron-diffraction patterns with lattice parameters close to the lattice parameters of these metals in a bulk state.

Average crystallite size depending on the layer thickness is varied in the range of 10-20 nm for Co, Fe and 20-50 nm for Cu, Ag (Fig. 1a, Fig. 2a). Individuality of the layers in the given systems at the layer thickness of $d_{Co,Fe}$ = 30-50 nm, $d_{Ag,Cu}$ = 10-40 nm remains even after annealing of the samples at the temperature of 700 K.

Results of the performed layer-by-layer analysis of the components of three-layer Co / Cu / Fe / S films show that insignificant interdiffusion (Fig. 3a and Fig. 4a) is observed in freshly condensed (irrespective of the layer thickness) samples. In accordance with the state diagram, limited solubility of the components is typical for the investigated film systems. Therefore, presence of the region of insignificant interdiffusion can be conditioned by the grain boundary diffusion and condensation-stimulated diffusion.

After thermal treatment of the samples with the specified thicknesses at T_{an} = 700 K we can observe further insignificant penetration of Co, Fe and Cu atoms into the neighboring layers (Fig. 3b), but systems remains three-layer one. It is possible to explain this fact, most probably, by both slight grain boundary diffusion and withdrawal of dopant atoms away from the grain boundaries into the crystallite volume. We should note that possibility of the formation of highly dispersed magnetic Co granules in nonmagnetic copper matrix is one of the peculiarities of the investigated systems (cobalt and copper based). Therefore, probably, granular Co state is partly realized in the annealed films in the central layer (non-magnetic sublayer). At the same time, at rather thick nonmagnetic sublayer (d_{Cu} > 10 nm) one can assert that individuality of separate layers substantially remains in the system.

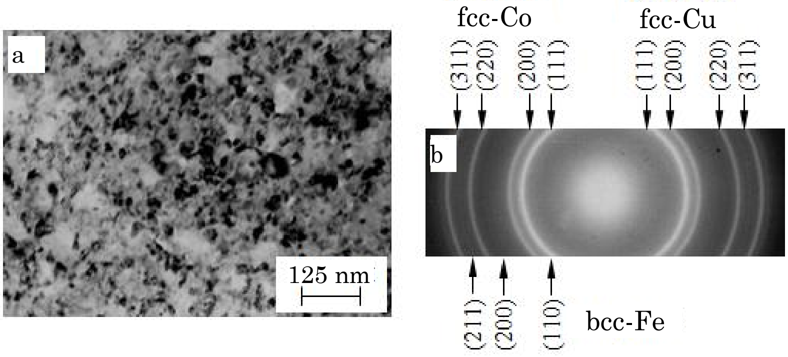

Fig. 1 – Crystal structure (a) and electron diffraction pattern (b) of the three-layer Co / Cu / Fe ($d_{Co,Fe}$ = 35 nm, d_{Cu} = 10 nm) film annealed at the temperature of 700 K

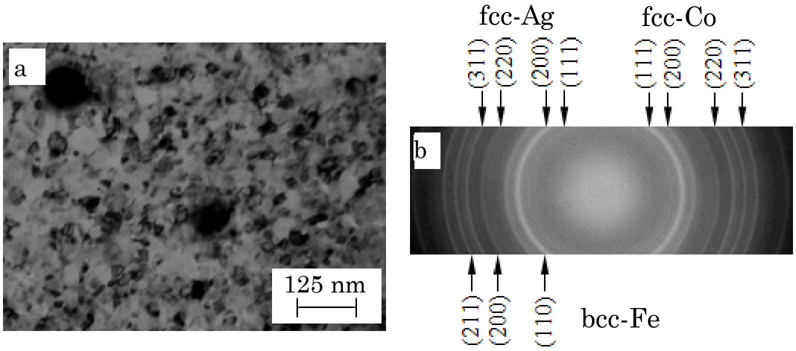

Fig. 2 – Crystal structure (a) and electron diffraction pattern (b) of the three-layer Co / Ag / Fe ($d_{Co,Fe}$ = 35 nm, d_{Ag} = 20 nm) film annealed at the temperature of 700 K

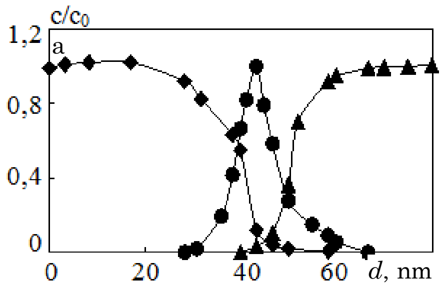

Fig. 3 – Diffusion profiles for Co(35 nm) / Cu(20 nm) / Fe(35 nm) / S films (♦♦♦ - Co, ●●● - Cu, ▲▲▲ - Fe) in the unannealed (a) and annealed at the temperature of 700 K (b) states (*c* is the concentration of the given element at the certain depth *x*, c_0 is the maximum concentration of the given element)

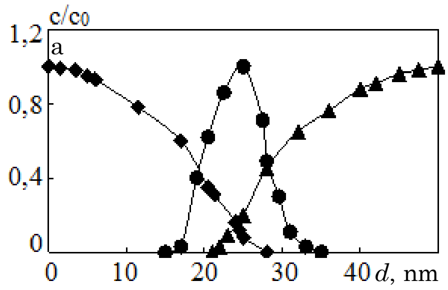

Fig. 4 – Diffusion profiles for Co(20 nm) / Cu(5 nm) / Fe(20 nm) / S films (♦♦♦ - Co, ●●● - Cu, ▲▲▲ - Fe) in the unannealed (a) and annealed at the temperature of 700 K (b) states (*c* is the concentration of the given element at the certain depth *x*, c_0 is the maximum concentration of the given element)

Usually, insignificant influence of the annealing on the behavior of diffusion processes is explained (see, for example, [8]) by diffusion saturation (on the stage of the upper layer condensation) of grain boundaries. This result qualitatively agrees with the data of the investigation of the phase composition, according to which both unannealed and annealed at $T_{an} = 700$ K films can be considered to be three-layer. Realization of the giant magnetoresistance effect in Co / Cu / Fe / S films annealed at the temperature of $T_{an} = 700$ K is one more proof of continuity of nonmagnetic sublayer there. But we have to note that total diffusion mixing of layers for the films with layer thickness of $d_{\text{Co,Fe}} = 10$-20 nm and $d_{\text{Cu}} < 5$ nm (Fig. 4b) is observed at the film annealing at $T_{an} = 700$ K. These results are also confirmed by the electron diffraction investigations.

In order to determine the effective diffusion coefficient *D* in the films we have used the Whipple relation [9]. Diffusion coefficients calculated for the film systems with Co, Fe and Cu components are equal to 10^{-18}-10^{-20} m^2/s. This value considerably exceeds the value of the volume diffusion coefficient for bulk samples with the same components (10^{-41} m^2/s). Most likely, the reason of this is the fact that diffusion in the films occurs, mainly, along the grain boundaries, their area is much larger and they are more defective than in bulk equilibrium samples.

Irreversible decrease in the sample electrical resistance due to the improvement of their structure (healing of defects, increase in the crystallite sizes) is observed in the annealing of the studied film samples.

This behavioral feature of the electrical resistance is also typical for single-layer films, for which the process of the healing of defects is described by the Wenda theory [10]. We have to note that substantial decrease in ρ as a result of annealing is also observed for three-layer films, in whose composition there are copper ($d_{\text{Cu}} = 2$-10 nm) or silver ($d_{\text{Ag}} = 2$-20 nm) layers. Their electrical resistance (annealing at the temperature of 700 K) decreases by 4-5 times. In the case of thicker nonmagnetic sublayers ($d_{\text{Cu}} > 10$ nm, $d_{\text{Ag}} > 20$ nm), only 2-3-fiold decrease in the resistance is observed after annealing at the temperature of 700 K.

Explanation of these differences in the decrease of electrical resistivity caused by annealing for the films with different thickness of nonmagnetic sublayers, to our opinion, should be searched in different degrees of the imperfection of Cu and Ag films; here one have to take into account the features of the diffusion processes there. Presence (or absence) of continuity of nonmagnetic sublayer also significantly influences the changes in the electrical resistivity.

Complete stabilization of the electrical properties is observed for the films annealed at $T_{an} = 700$ K during 30 min. In the sequel, unless specific warnings are made, graphs will be presented only for the films which underwent the corresponding thermal treatment.

Temperature dependences of the electrical resistivity and TCR for Co / Ag / Fe and Co / Cu / Fe films are shown in Fig. 5 and Fig. 6. Quadratic in temperature dependence $\rho(T)$, which is most probably conditioned by the electron-magnon interaction, is fixed in the temperature range of 150-600 K. However, it should be noted that in the framework of the achieved experimental accuracy, it is difficult to determine a concrete behavior of the dependence $\rho(T)$.

Our measuring accuracy does not allow to reveal on the dependences β(T) for three-layer films the features connected with the characteristic points (Debye temperature $T_D(\text{Co}) = 445$ K, $T_D(\text{Ag}) = 225$ K, $T_D(\text{Cu}) = 343$ K, $T_D(\text{Fe}) = 467$ K and temperatures $\theta_1 = 590$ K (transition

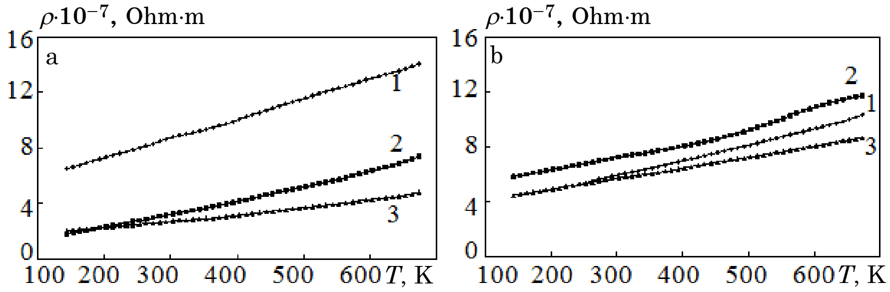

Fig. 5 – Temperature dependence of the resistivity for annealed at T_{an} = 700 K films: a – Co / Ag / Fe / S (1 – $2d_F$ = 40 nm, d_N = 10 nm; 2 – $2d_F$ = 70 nm, d_N = 15 nm; 3 – $2d_F$ = 50 nm, d_N = 20 nm) and b – Co / Cu / Fe / S (1 – $2d_F$ = 70 nm, d_N = 4 nm, 2 – $2d_F$ = 40 nm, d_N = 6 nm; 3 – $2d_F$ = 60 nm, d_N = 20 nm)

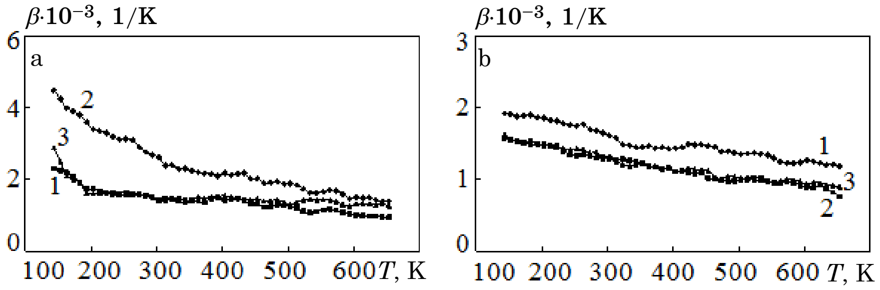

Fig. 6 – Temperature dependence of the TCR for annealed at T_{an} = 700 K films: a – Co / Ag / Fe / S (1 – $2d_F$ = 40 nm, d_N = 10 nm; 2 – $2d_F$ = 70 nm, d_N = 15 nm; 3 – $2d_F$ = 50 nm, d_N = 20 nm); b – Co / Cu / Fe / S (1 – $2d_F$ = 70 nm, d_N = 4 nm; 2 – $2d_F$ = 40 nm, d_N = 6 nm; 3 – $2d_F$ = 60 nm, d_N = 20 nm)

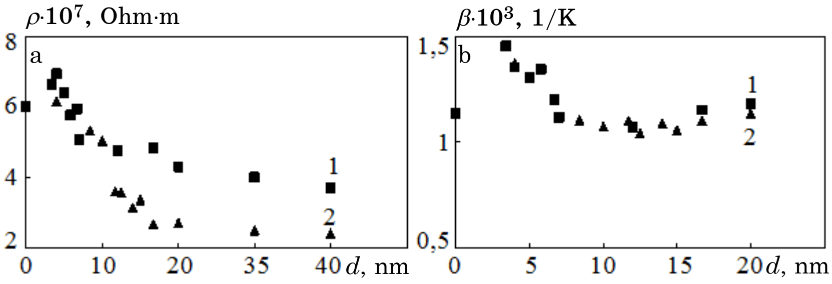

Fig. 7 – Dimensional dependence of the electrical resistivity (a) and TCR (b) for three-layer film systems: 1 – Co / Cu / Fe / S and 2 - Co / Ag / Fe / S ($d_{Co} = d_{Fe}$ = 30 nm)

from $\rho \sim T^2$ to $\rho \sim T$) and θ_2 = 180 K (transition from $\rho \sim T^3$ to $\rho \sim T^2$)) [11, 12]. If anomalies exist there, they do not exceed the values of 0.1-0.2·10^3 K^{-1}.

In Fig. 7 we represent the experimental dependences of the resistivity and TCR on the sublayer thickness d_N obtained at room temperature. Point on the ordinate axis (d_N = 0) corresponds to two-layer Co / Fe film. As seen, in the case of small effective thicknesses of nonmagnetic sublayer (d_N < 10 nm) maximum of the dependence $\rho(d_N)$ is weakly expressed that, most probably, is conditioned by the diffusive behavior of the interaction of conduction electrons with conductor interfaces and structural discontinuity of the sublayer. At further increase in d_N the dependence monotonously decays. Dependences $\beta(d_N)$ also have nonmonotonic behavior by the same reasons.

4. CONCLUSIONS

Three-phase fcc-Co, Cu, Ag and bcc-Fe composition is fixed on the electron diffraction patterns for annealed at the temperature of 700 K three-layer Co / Ag / Fe and Co / Cu / Fe films with d_N = 5-40 nm.

Investigations of the diffusion processes performed by the SIMS method for unannealed and annealed at the temperature of 700 K Co / Cu / Fe / S film samples have shown that individuality of the layers remains in freshly condensed films with $d_{Co,Fe}$ = 10-50 nm, d_{Cu} = 3-20 nm. Annealing at T_{an} = 700 K of the samples with $d_{Co,Fe}$ = 10-20 nm and d_{Cu} = <5 nm leads to a complete diffusione mixing.

Individuality of the layers remains in Co / Cu / Fe systems at the layer thickness of $d_{Co,Fe}$ = 30-50 nm and d_{Cu} = 10-40 nm after annealing at the temperature of 700 K.

Dependences of the electrical resistivity and TCR on the thickness of copper sublayer are nonmonotonic that, to our opinion, is connected with the diffusive behavior of the conduction electron scattering by conductor interfaces.

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