Structural, Magnetic and Magnetoresistive Properties of Ternary Film Ni-Fe-Co Alloy

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The results of the experimental studies of the structural and phase state, magnetic and magnetoresistive properties of Ni-Fe-Co alloy thin films with the initial components concentration of cNi = 40, cFe = 10, and cCo = 50 at.% in the annealing temperature range of ΔT = 300-1000 K are presented. It is shown that as-deposited alloy films have a two-phase fcc-NiFe + hcp-Co structure. The fcc-phase with the lattice parameter of 0.354 nm, which corresponds to Ni-Fe-Co solid solution, is observed after heat treatment at 900 K. Thin films based on Ni-Fe and Co exhibit anisotropic magnetoresistance with the highest value (0.35%) observed in the perpendicular measurement geometry. The value of magnetoresistance tends to rise with increasing annealing temperature. The results of the magnetic and magnetoresistive measurements indicate that the easy axis of magnetization is parallel to the sample plane.

Keywords: Magnetoresistive properties, Magnetoresistance, Hysteresis, Magnetic anisotropy, Coercive force, Magnetization axis, Saturation field.

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1. INTRODUCTION

Currently a great attention is devoted to the investigation of the physical properties of 3d-metal thin films of and structures on their base. Use of ferromagnetic alloys as elements of the structures which exhibit the anisotropic (AMR), giant (GMR) or tunnel magnetoresistance makes them the actual object of study. An important practical task is to obtain thin-film systems characterized by high saturation field (~ 2 T), low coercivity, small magnetostriiction, easy controllability of anisotropy at small field, significant magnetic moment and thermal stability in a wide temperature range [1-2].

Soft magnetic Ni-Fe alloys are known because of a wide application of their magnetic, magnetostrictive and magnetoresistive properties in the production of sensitive elements of sensor technique, for example, in magnetic heads or high-sensitive devices [3-4]. Depending on the composition, the authors of the works [5-7] single out three concentration regions in which Ni3Fe and Ni-Fe phases are stabilized at the concentration of Fe atoms (cFe) to 50 at.% (permalloy alloys), invar at cFe to 64 at.%, and Ni-Fe α-phase at cFe ≥ 75 at.%.

For today, structural as well as magnetic and magnetoresistive properties of permalloy alloys have been studied in detail. Thus, for example, the authors of [7-8] have shown the influence of the component concentrations and annealing temperature on the phase composition of the films, in particular, formation of the Ni-Fe and Ni3Fe fcc-phases, the latter of which, according to the work [9], is characterized by low magnetocrystalline anisotropy and magnetostriiction close to zero. In this case, investigations of the properties of heterogeneous ferromagnetic alloys based on Ni-Fe and Co, as a soft magnetic material, which is able to have stable characteristics for practical application in nanoelectronics, remain promising. Therefore, the aim of the present work was to establish the correlation between structural and phase state, magnetic and magnetoresistive properties at different annealing temperatures of thin film samples based on Ni-Fe and Co.

2. EXPERIMENTS

Thin film samples of the Fe, Ni and Co-based alloy were obtained by the thermoresistive co-evaporation technique using two independent sources: permalloy 79 NM (79-80 wt. % of Ni, 2-5 wt. % of Mo, 13-16 wt. % of Fe) and Co in the HV chamber VUP-5M with the residual gas pressure of 10–4 Pa with further deposition on the amorphous glass ceramic substrate (ST-50-1-1-0.5) for the investigation of the magnetic and magnetoresistive properties and on copper grids with pre-deposited carbon layer for the study of the structure and phase composition. Substrate temperature was equal to 300 K and condensation rate ~ 1-5 nm/s. Film thickness (d) was measured using optical interferometer MII-4 and was equal to 37 ± 1 nm. Chemical composition of the obtained alloy was calculated proceeding from the mass of components, used for deposition, and additionally controlled by the method of energy-dispersive X-ray (EDX) spectroscopy with measurement accuracy of ± 5 %.

For the analysis of the thermal treatment influence on the structural, magnetic and magnetoresistive properties, the samples were annealed in vacuum to T = 500, 700, 900 and 1000 K during 20 min. Investigation of the structural and phase state was carried out using the transmission electron microscope TEM-125 K.

Study of the magnetoresistive properties was carried out using the automated complex by the standard four-probe method [10] at flowing electric current in the direction parallel to the plane of the film system in three geometries: perpendicular (magnetic field lines are perpendicular to the sample plane and direction of the current flow); transverse (magnetic field lines are parallel to the sample plane and perpendicular to the direction of the current flow) and longitudinal (magnetic field lines are parallel to the sample plane and direction of the
current flow). The value of the magnetoresistance (MR) $\Delta R / R_s$ (%) was calculated by the following relation: $\Delta R / R_s = [(R(B) - R_s) / R_s] * 100$ %, where $R_s$ is the electrical resistance in the magnetic saturation field or in the maximally possible magnetic field; $R(B)$ is the current value of the film resistance in magnetic field.

Vibrating-sample magnetometer VSM Lake Shore Model 7400 (Jean Lamour Institute, University of Lorraine, Nancy, France) was used for the study of the magnetic characteristics of the samples. Measurements were performed in two geometries, namely, “in plane” (magnetic field lines are parallel to the sample plane) and “out of plane” (magnetic field lines are perpendicular to the sample plane), and also with the change in the angle between the sample plane and magnetic field from 0 to 90 degrees.

3. CRYSTAL STRUCTURE AND PHASE COMPOSITION

Since bulk alloy permalloy 79 NM was one of the initial materials for obtaining samples based on Ni-Fe and Co, then mismatch of the chemical composition of alloy to the initial one, which is induced by the fractionation, can be observed during film condensation [11]. In Fig. 1 we show the EDX-results of the chemical composition of the initial Ni-Fe alloy (see Fig. 1a), thin film sample on its base (Fig. 1b) and thin film sample based on Ni-Fe and Co (Fig. 1c).

![Fig. 1 – EDX-spectra for the initial alloy 79 NM (a), Ni-Fe (b) and Ni-Fe-Co (c) film alloys. Concentration of the components, at. %: c_{Ni} = 22, c_{Fe} = 76, c_{Co} = 2 (for bulk sample); c_{Ni} = 20, c_{Fe} = 80 (for thin film Ni-Fe sample); c_{Ni} = 10, c_{Fe} = 40, c_{Co} = 50 (for thin film Ni-Fe-Co sample)

Spectra processing shows that composition of the obtained films slightly differs from the composition of bulk alloy 79 NM. Distinction in concentrations of the components in the expected and obtained samples can be explained by the difference in the saturated vapor pressures of Ni and Fe atoms. Character peaks in the left part of the spectrum for the film samples (Fig. 1b, c) correspond to the amorphous glass ceramic substrate. Absence of molybdenum is also observed on the energy-dispersive spectra for Ni-Fe films and samples based on Ni-Fe and Co that can be connected with infusibility of molybdenum and, as a result, with its small evaporation rate. According to the EDX-results, the studied Ni-Fe-Co film samples have the following chemical composition in at. %: $c_{Ni} = 40$, $c_{Fe} = 10$ and $c_{Co} = 50$.

TEM investigations of the thin film Ni-Fe ($c_{Ni} = 80$, $c_{Fe} = 20$) samples have shown that in the as-deposited state the films are fine dispersed (the average crystallite size is less than 5 nm) [12] and they also have the so-called labyrinthine structure that is typical for ferromagnetic materials and conditioned by disorder of domains [13]. Annealing to the temperature of 900 K leads to a gradual increase in the crystallite size.

According to the literature data [14], the bulk Ni-Fe alloy has the fcc-lattice and parameter, which varies in the range from 0.3524 to 0.3596 nm. Investigations of the phase composition of the thin film samples obtained from the bulk permalloy 79 NM in the annealing temperature range of 300-900 K (Fig. 2), which were carried out in the work [12], have shown that their phase composition corresponds to the fcc-NiFe phase with the lattice parameter $a$ (Ni$_3$Fe) = 0.353-0.355 nm which is close to the tabulated value of the lattice parameter of intermetallic Ni$_3$Fe phase (structural CusAu type), which, according to the works [8, 15], is equal to $a$ (Ni$_3$Fe) = 0.354 ± 0.001 nm and $a$ (Ni$_3$Fe) = 0.355 nm, respectively.

In Fig. 2 we illustrate the typical electron diffraction patterns and micrographs of the crystal structure of the Ni-Fe-Co/Sub thin film samples with 37 nm thickness. Analysis of the presented in Fig.2 results has shown that the films after deposition, as in the case of single-component permalloy and Co films, have the fine dispersed structure with the average grain size $L = 6-7$ nm. During thermal treatment, one can observe a gradual growth of crystallites and at $T_a = 900$ K (Fig. 2b) there is a 4-5-fold increase in the grain size ($L = 25-30$ nm). Annealing temperature increasing to 1000 K leads to the formation of large conglomerates of crystallites, whose size reaches 70-80 nm (Fig. 2c). Phase composition of the samples after condensation corresponds to the fcc-NiFe+$\text{hcp-Co}$ with the lattice parameter $a$ (Ni$_3$Fe) = 0.354 nm and $a$ (hcp-Co) = 0.242 nm, respectively. ($a_{0}(\text{Ni}_3\text{Fe}) = 0.3545 \text{ nm}; a_{0}(\text{hcp-Co}) = 0.2505 \text{ nm}$ [16]). At annealing to 500 and 700 K changes in the phase composition are not observed, while at $T_a = 900$ K only lines which belong to the fcc-phase with the lattice parameter $a = 0.354$ nm are present on the electron diffraction patterns. According to the data of the work [5], in the Ni-Fe-Co system at the concentration of the components of 40, 10 and 50 at. %, respectively, and at 900 K, the alloy is characterized by the presence of single-phase composition, which corresponds to the fcc-lattice. Thus, during annealing at 900 K formation of the unordered solid solution with the fcc-lattice occurs on the basis of three-component Ni-Fe-Co alloy. Moreover, weak lines with the interplanar spacings $d_{200} = 0.215$ nm and $d_{220} = 0.150$ nm, which belong to the oxide FeO (see Fig. 2b) are present on the electron diffraction patterns. At $T_a \geq 1000$ K changes
in the phase composition are not observed. Only a slight increase in the lattice parameter to 0.355 nm takes place. Lines with the interplanar spacings $d_{311} = 0.250$ nm and $d_{220} = 0.145$ nm (Fig. 2c), which belong to the oxide Fe$_3$O$_4$ [16], also appear on the electron diffraction patterns.

4. MAGNETIC AND MAGNETORESISTIVE PROPERTIES

Ferromagnetic materials and alloys on their base are characterized by the anisotropic magnetoresistive properties. AMR depends on the direction of spontaneous magnetization and is connected with the rotation of ferromagnetic domains depending on the applied magnetic field [17].

Magnetization processes in ferromagnetic materials are, mainly, defined by three types of interaction: exchange interaction, magnetocrystalline anisotropy and magnetic dipole interaction. Minimization of the total magnetic energy determines the stable configuration of magnetization. From the point of view of the practical application, remagnetization at the coercive field $B_c$ is one of the interesting processes [18]. Measurements of the magnetoresistance of ferromagnetic materials allow to investigate the remagnetization mechanisms. Magnetoresistance, in total, is a sum of four components, namely, usual [19] and anisotropic MR [17], usual and anomalous Hall effects [20]. In the case of easy magnetization in the plane and applied “in plane” field, anisotropic magneto-resistance makes the largest contribution to the MR value. Moreover, the influence of domain walls on the MR value should be also taken into account [21].

Investigations of the magnetoresistive properties of thin film Ni-Fe-Co samples have shown that the given system, as it was noted earlier, displays the anisotropic character of magnetoresistance. Dependences of the resistance on the magnetic field are represented in Fig. 3. As seen from the figure, the largest values of $\Delta R/R_s$ and $B_c$ correspond to the perpendicular measurement geometry and are equal to 0.35 % and 29 mT, respectively. In addition, for the specified geometry the absence of the saturation field is observed for as-deposited and annealed at 500 and 700 K samples; saturation of MR appears only after thermal treatment at 900 K and is equal to ~200 mT that 3-4 times (depending on the annealing temperature of the samples) exceeds the value of the saturation field for the transverse measurement geometry. The given results imply the presence of hard remagnetization axis exactly in this geometry. The reason of this is the domination of shape anisotropy, when orientation of magnetization vectors in the film plane is energetically more favorable in the absence of magnetic field. Based on this, for film remagnetization along the normal, it is necessary to apply to film plane the magnetic field, whose induction is much larger than under the condition, when film is remagnetized in the plane. In our case, easy remagnetization is observed for the field orientation pa-
rallel to the sample plane.

Absence of the saturation field at the perpendicular measurement geometry can be explained by the fact that in the case, when magnetic field \( B \) makes a certain angle \( \alpha \) with the easy magnetization axis, field pressure on a domain wall decreases, i.e. it will be defined by the field component \( B \cos(\alpha) \) and at \( \alpha = 90^\circ \) (\( B \) is perpendicular to the sample plane) a wall will not be shifted and sample remagnetization occurs by the rotation of the total spontaneous magnetization vector \( M_s \). If apply magnetic field along the normal to the easy magnetization axis (in the given case, to the sample plane), orientation of \( M_s \) will be determined by the competition of two energies: magnetic anisotropy energy \( E_A \), because of which \( M_s \) tends to orient along the easy magnetization axis (in the sample plane) and energy of the magnetized sample in magnetic field \( E_B \), because of which \( M_s \) tends to orient along the field \( B \) (along the normal to the sample plane) [22]. Absence of the saturation field \( B_s \) implies that \( E_B \) and, therefore, \( B \) has insufficient value for the rotation of magnetization vector \( M_s \) along the applied magnetic field. Thus, changes in the ratio of \( E_B \) and \( E_A \) energies in connection with the formation of unordered solid solution based on three-component Ni-Fe-Co alloy that influenced the magnetic characteristics of the studied sample are the reason of the fact that after annealing at 900 K saturation of the magnetoanisotropy is observed within the applied field.

Nature of the magnetoresistive dependences for the as-deposited and annealed films correlates well with the structural changes during thermal treatment of the samples. Decrease in the MR value for the perpendicular and transverse measurement geometries after annealing at 500 K is connected with heating of defects and behavior of thermostabilization processes which can induce changes in the sample domain structure.

Further thermal treatment at 700 K did not induce considerable changes in magnetoanisotropy, except insignificant increase in the MR value at the transverse measurement geometry from 0.05 % to 0.08 %. Not only the increase in the MR value (almost 4-fold increase), but also the appearance of a step at the field of 0-20 mT are the characteristics of the magnetoresistive curve at the perpendicular measurement geometry after thermal treatment at 900 K. Substantial increase in the magnetoanisotropy and changes in the behavior of the magnetoresisive dependences after thermal treatment at 900 K can be explained by the phase changes in the thin film Ni-Fe-Co sample.

Investigation of the magnetic properties using vibrating-sample magnetometer has shown that samples before thermal treatment exhibit an insignificant anisotropy in the plane (Fig. 4). For polycrystalline samples the given phenomenon can be explained by the appearance in the thin film of the regions with prevalent direction of crystallite growth that is connected with the sample production technique. We have to note that after annealing at 900 K anisotropy is not observed as a result of the recrystallization processes and, possibly, for formation of the unordered solid solution based on three-component Ni-Fe-Co alloy.

In Fig. 5 we present the typical magnetic hysteresis for as-deposited and annealed to 900 K samples. For the sample orientation parallel to magnetic field hysteresis loops have almost the rectangular shape with sharp remagnetization. Magnetization of the films is completely changed in the range of \( \pm 13 \) mT in as-deposited and \( \pm 23 \) mT in the annealed to 900 K states. Rectangular form of the hysteresis (Fig. 5, curves 1) is typical for easy magnetization which indicates that easy magnetization axis is oriented parallel to the sample plane. Obtained results are close to the experimental investigations of permalloy and Co in the works of W. Weber et al. [23-25]. Difference in the shape of hysteresis loops with sample rotation relative to the magnetic field is explained by the change in the remagnetization process. Thus, view of the hysteresis loop and main parameters (magnetization, coercive force) mostly depend on the field orientation with respect to the easy magnetization axis,
i.e. to some angle $\alpha$. Dependence $B_c(\alpha)$ or, in other words, anisotropy of the coercive force in comparison of its theoretical and practical values gives the possibility to determine which process makes the greatest contribution to the magnetic hysteresis: propagation of domain walls or rotation of spontaneous magnetization [22]. At the rotation of the sample by an angle from $0$ to $85^\circ$ there is the increase in the coercive force $B_c$ (typical dependence is shown in Fig. 6), whose relative change is equal to 67 % for the film before thermal treatment and 81-82 % after it irrespective of the annealing temperature. In Fig. 7 we present the normalized hysteresis $M/M_s$ for as-deposited and annealed to different temperatures (Ni-Fe-Co)/Sub samples of the thickness of 37 nm at the “in plane” orientation of magnetic field. As Fig. 7 shows there is a clear increase in the value of residual magnetization, coercive force and saturation field with the annealing temperature increasing.

Relative change of $B_s$ and $B_c$ in the annealing temperature range of 300-900 K is equal to 154 % and 88 %, respectively. Increase in the saturation field $B_s$ in the case of ferromagnetic alloys is reached after finishing the remagnetization processes, namely, the growth of domains with the magnetic moment oriented in the direction of the easy magnetization axis as a result of the propagation of domain walls and rotation of the sample magnetization vector in the direction of magnetizing field [26-27].

5. CONCLUSIONS

In the given work we present the results of the experimental investigations of the structural and phase state, magnetic and magnetoresistive properties of the (Ni-Fe-Co)/Sub film systems in the as-deposited and annealed to 500, 700, 900 and 1000 K states.

Having analyzed the experimental data it is established that as-deposited samples have two-phase fcc-NiFe + hcp-Co composition and finely dispersed structure. Annealing of the samples in the temperature range of $\Delta T_a = 500$-700 K does not lead to the considerable changes in the structure and phase composition. Only one fcc-phase with the lattice parameter $a = 0.354$ nm, which belongs to Ni-Fe-Co solid solution, is fixed after thermal treatment at 900 K.

Magnetoresistance of the investigated structures has anisotropic character. Maximum MR and $B_c$ values correspond to the perpendicular measurement geometry and are equal to $0.35 \%$ and 29 mT, respectively. Influence of annealing on the magnetic properties is manifested in the disappearance of anisotropy in the sample plane, increase in the coercivity and saturation field with the increase in the treatment temperature. Relative change of $B_c$ and $B_s$ in the temperature range of $\Delta T_a = 300$-900 K is equal to 154 % and 88 %, respectively.

The results obtained in the present work correlate among themselves and imply the significant effect of the formation of unordered solid solution based on three-component Ni-Fe-Co alloy on the magnetic and magnetoresistive properties of the investigated samples.

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