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Evolution of magnetic and magnetoresistive properties of sputtered NiFe/Cu/Co/Cu nanostructures under ageing and annealing

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Magnetic and magnetoresistive properties of sputtered $Ni_{80}Fe_{20}$(4–6 nm)/Cu(2–10 nm)/Co(2 nm)/Cu(2 nm) nanostructures have been studied after room temperature ageing and thermal annealing at 75–150°C. Magnetic properties of Co/Cu bilayer and NiFe/Cu one were investigated. The transformations of field dependences of magnetoresistance, and the nanostructure hysteresis loops have been considered. The evolution of characteristics in the nanostructure as a whole is supposed to be due to changes in magnetic properties of the upper Co/Cu layer, namely, to the magnetic anisotropy deterioration and the appearance of separate single-domain and superparamagnetic particles.

Исследованы магнитные и магниторезистивные свойства наноструктур $Ni_{80}Fe_{20}$(4–6nm)/Cu(2–10 nm)/Co(2 nm)/Cu(2 nm), изготовленных методом ионно-плазменного распыления, после временной выдержки при комнатной температуре и отжига в интервале температур 75–150°C. Исследованы магнитные свойства бислоев Co/Cu и NiFe/Cu. Проведен анализ трансформаций полевых зависимостей магнитосопротивления и петель гистерезиса наноструктур. Предложено объяснение эволюции характеристик наноструктуры как результат изменения магнитных свойств верхнего слоя Co/Cu, а именно, разрушения в нем магнитной анизотропии, а также появлением изолированных однодоменных и суперпарамагнитных частиц.

The spin-valve nanostructures consisting of two ferromagnetic layers and a non-magnetic spacer are studied intensively from the viewpoint of their applicability in spin-electronic devices (e.g., as magnetically tunable parts of transistors [1, 2]) as well as in high-density recording technology [3]. An important aspect of such investigations is the study of magnetic properties stability. As a rule, the multilayered films produced by the ion-plasma sputtering technologies are nonequilibrium systems with various structure defects caused by large length of grain boundaries and technological gas impurities. Moreover, the contact of dissimilar materials may cause stresses and diffusion. The tendency to thermodynamic equilibrium stimulates the various relaxation processes in nanostructures that may influence their performance characteristics either positively or negatively. In this work, we have investigated the thermal stability of magnetic and magnetoresistive properties of nanostructures consisting of combination of Permalloy, cobalt, and copper nanolayers. Spin valve structures including these materials are of considerable promise since it is possible to operate their electrical resistance by relatively low magnetic fields. We have studied comprehensively the variations in field dependences of magnetoresistance and hysteresis loops during ageing and annealing in the temperature range of 75–150°C.

The nanostructures of substrate/NiFe/Cu/Co/Cu configuration have been studied. The nanostructures were produced using a combination of two methods, the triode ion-plasma sputtering for deposition of Co and NiFe layers and magnetron sputtering for Cu deposition. The details of film preparation are described in [4]. The deposition rates of Co, NiFe and Cu were 0.043, 0.04 and 0.19 nm/s, respectively. The substrate temperature during the deposition did not exceed 50°C. When magnetic layer were deposited, the auxiliary magnetic field of about 30 Oe was applied in the film plane. The thickness of NiFe layer (t_{NiFe}) was 4–6 nm, that of Co layer (t_{Co}) was 2 nm. The Cu layer thickness (t_{Cu}) after preliminary experiments with t_{Cu} = 1, 2.0, 2.7, and 10 nm was chosen to be 2.7 nm, since it ensures highest magnetoresistive ratio value (see below) in as-prepared state.

In addition to the nanostructures, the individual Co and NiFe films with and without coating Cu layer have been studied.

A high sensitivity vibrating sample magnetometer was used to measure the magnetization curves. The mean magnetization values of nanostructures and individual films were determined by comparing the signals from the sample under investigation and from a reference sample taking into account the total thickness of magnetic layers and the sample area. These measurements were carried out in magnetic fields up to 250 Oe applied in the film plane both along and normal to the auxiliary field direction.

The magnetoresistive characteristics, such as the maximum magnetoresistive ratio $(\Delta R/R)_{max} = (R_{max} - R_s)/R_s$ (where R_{max} is the maximum resistance value; R_s, the resistance value at the strongest field used) and field dependences of magnetoresistance ($(\Delta R/R) = f(H)$) were measured for strip-shaped samples of 20 mm×1 mm size at in-plane magnetic fields up to 1 kOe both parallel and perpendicular to the operating current.

The films were subjected to ageing at room temperature and annealing in temperature range of 50–150°C in air.

The field dependences of magnetoresistance $\Delta R/R = f(H)$ for as-prepared nanostructures of $Ni_{80}Fe_{20}$(4.8 nm)/Cu(2.7 nm)/Co(2 nm)/Cu(2.7 nm) configuration are shown in Fig. 1a, b. The shapes of these curves are seen to differ noticeably for cases of parallel and perpendicular orientation of the applied magnetic field relative to the operating current direction. The $\Delta R/R = f(H)$ dependence measured in the field along the current includes a section where the resistance drops in low fields (from +5 Oe to

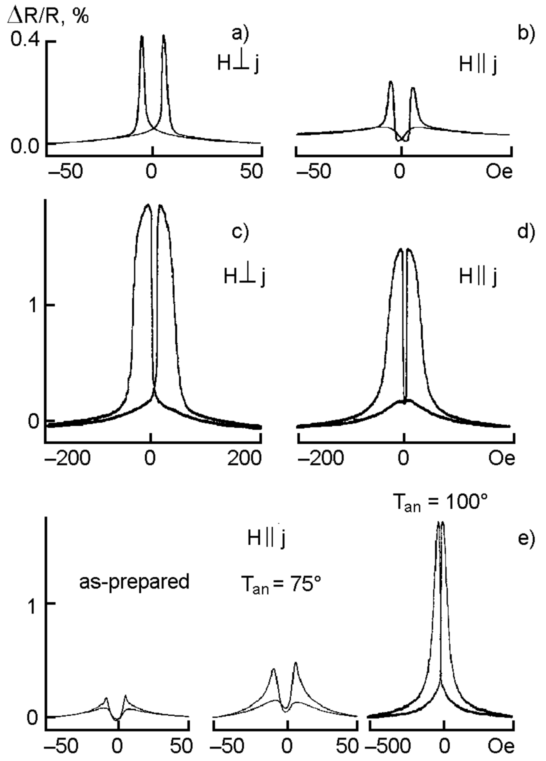

Fig. 1. Field dependences of magnetoresistance for NiFe(4.8 nm)/Cu(2.7 nm)/Co(2 nm)/Cu(2.7 nm) nanostructures in as-prepared state (a,b), where (a) field **H** is perpendicular to current **j**, (b) field **H** is parallel to current **j**; the same after ageing at room temperature during 12 months (c, d); after annealing in temperature range up to 100C (**H** is parallel to **j**) (e).

−2 Oe). This indicates that we observe an anisotropic magnetoresistance (AMR) due to the regions where magnetization direction is normal to the operating current arising in the nanostructure. Moreover, this effect is to occur in NiFe layer only, since it was found that the magnetization reversal of Permalloy layer occurs in low fields (see below) and the AMR value of Co is lower than that of NiFe. The magnetoresistance increasing observed in reverse fields exceeding 5 Oe is connected with giant magnetoresistance effect (GMR) [5]. This effect is known to be observed in layered nanostructures if the magnetization vectors ($\mathbf{I}_S$) of neighboring layers separated by nonmagnetic interlayers are noncollinear and maximum GMR value is attained at antiparallel $\mathbf{I}_S$ orientations. The maximum magnetoresistive ratio $(\Delta R/R)_{max}$ in as-prepared state for the samples under study was 0.2–0.4 %.

After long-term ageing at room temperature, the shape of field dependences of magnetoresistance was changed essentially (see

Fig. 1c,d). $(\Delta R/R)_{max}$ increased to 1.1–1.3 % in 3 months and to 1.9–2.0 % in 12 months. The same behavior of magnetoresistive properties was observed after a short-term annealing (t = 1 h) at temperature of 50–150°C (Fig. 1e). When the ageing time increases or annealing temperature rises, the differences in shape of $\Delta R/R = f(H)$ curves measured along and perpendicular to the operating current were faded gradually. The field of the magnetoresistance maximum H_{max} was increased from 5–6 Oe to 10–15 Oe, the hysteresis region was extended and the saturation field rised (up to >1000 Oe after annealing at 150°C).

To reveal the reasons for transformations of $\Delta R/R = f(H)$ dependences, we have measured the magnetic characteristics in as-prepared state and after annealing for individual Co and NiFe films as well as for various layered combinations made up of above-mentioned ferromagnetic films and Cu layers.

The magnetic characteristics of individual NiFe and Co films depend on their thickness in the range from 1 nm to 10 nm. To obtain the nanostructures, the films with the largest difference in coercive force values were selected. Those are NiFe films of 4.8 nm thickness and Co films of 2 nm one. The Permalloy films were characterized by low coercive force $H_C \approx 0.5$–0.6 Oe and the saturation magnetization value $I_S \approx 750$–780 G which was close to that of bulk $Ni_{80}Fe_{20}$. Easy axes (EA) of films were directed along the auxiliary magnetic field. Cobalt films of 2 nm thickness had $H_C \approx 52$–54 Oe and $I_S \approx 800$–1000 G. EA direction coincided with the auxiliary field direction, too. After annealing in at 50–150 °C, the magnetic characteristics of individual films did not change essentially.

When NiFe, Co, and Cu layers were combined into a sandwich-type nanostructure, the magnetic parameters of each magnetic layer depended on Cu interlayer thickness. Fig. 2a, b shows the shapes of hysteresis loops for $Ni_{80}Fe_{20}$(4.8 nm)/Cu(t_{Cu})/Co(2 nm)/Cu(2.7 nm) nanostructures with t_{Cu} = 2.7 nm and $t_{Cu} \approx 10$ nm, respectively. In the case of "thick" interlayer (≈ 10 nm), there is a distinct "step" in the hysteresis loop. Its location evidences that NiFe and Co films are magnetized independently keeping the parameters peculiar to individual films. This assumption has been verified by fitting of experimental hysteresis loops supposing that the total nanostructure magnetization is the weighted sum of each layer magnetization at the specified field value. To describe the hysteresis loop for each layer, we have used the functionwhich was the best approximation of hysteresis loops for individual Co and NiFe film under study:

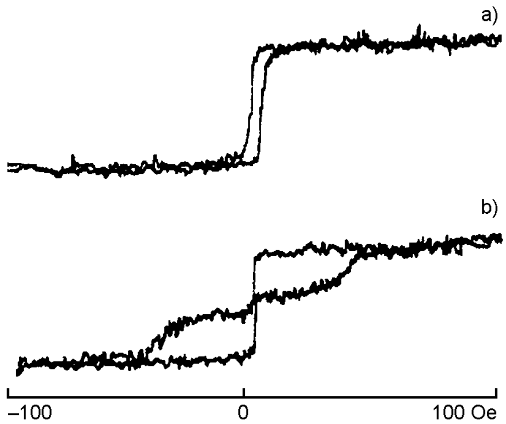

Fig. 2. Hysteresis loops of NiFe(4.8 nm)/Cu(2.7 nm)/Co(2 nm)/Cu(2.7 nm) nanostructures (a) and NiFe(4.8 nm)/Cu(10 nm)/Co(2 nm)/Cu(2.7 nm)

$$\frac{I}{I_s} = \tanh\left(\frac{H \pm H_c}{H_c}\tan\left(\frac{\pi \cdot s}{2}\right)\right), \qquad (1)$$

where H is the external field; H_C, the coercive force; s, the value approximately equal to remanence ratio I_r/I_S.

When the Cu thickness was small (t_{Cu} = 2.7 nm), the interlayer coupling influences the magnetization reversal in each layer. As follows from the hysteresis loop consideration (Fig. 2a), the coercive force of NiFe layer increases and that of Co layer decreases. The nanostructures have revealed the in-plane anisotropy. It is interesting to note that sometimes, the remanence ratio of hysteresis loop measured perpendicular to the auxiliary field was greater than that for parallel field orientation. In what follows, the direction with greater I_r/I_S will be referred to as the conventional EA one.

To reproduce the shape of experimental hysteresis loop by fitting, we took the thickness and saturation magnetization of NiFe and Co layers as t_{NiFe} = 4.8 nm, I_S^{NiFe} = 750 G, t_{Co} = 2 nm, I_S^{Co} = 1000 G, respectively, and varied values of H_C and s. A good agreement of calculated loop with experimental one measured along conventional EA was found at H_C^{NiFe} = 1.5 Oe and H_C^{Co} = 6 Oe. The calculated total saturation magnetization coincided with the nanostructure

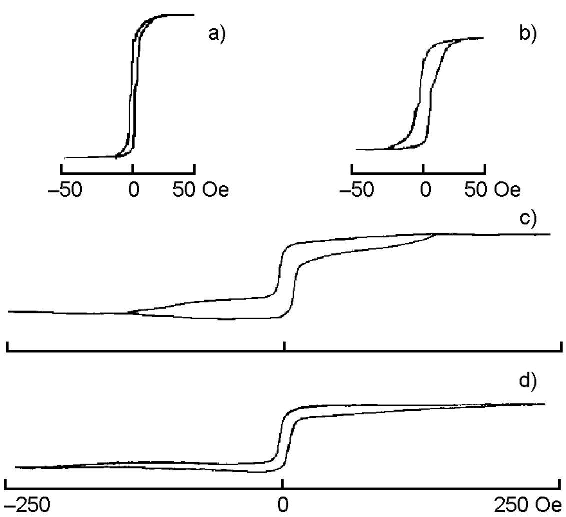

Fig. 3. Evolution of hysteresis loops of NiFe(4.8 nm)/Cu(2.7 nm)/Co(2 nm)/Cu(2.7 nm) nanostructures under thermal annealing. As prepared state (a), T_{an}= 75°C (b), T_{an}= 100°C (c), T_{an} =125°C (d).

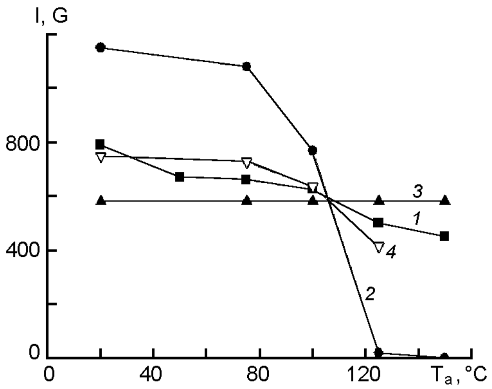

Fig. 4. Experimental dependences of the mean magnetization I for NiFe(4.8 nm)/Cu(2.7 nm)/ Co(2 nm)/Cu(2.7 nm) nanostructure measured in H = 250 Oe on the annealing temperature T_a (*1*) and calculated dependence (*4*) obtained by combining of similar experimental dependences for Co/Cu bilayer (*2*) and NiFe/Cu bilayer (*3*) taking into account their volume contributions.

magnetization measured in $H = 250$ Oe ($I_S \approx 800$ G).

During annealing, the shape of hysteresis loops was transformed gradually (Fig. 3). The part of hysteresis loop characterizing the layer with higher coercivity expanded along H-direction. But contribution of this layer to the total system magnetization decreased and after 150°C annealing became essentially imperceptible. The mean magnetization of nanostructures (measured at H = 250 Oe) decreased with rising annealing temperature, too. It drops from I_S = 790–800 G in as-prepared state to I_S = 500–520 G after 150°C annealing (see Fig. 4).

When comparing the behavior of magnetic and magnetoresistive characteristics, it is convenient to distinguish three temperature range of annealing where the specific peculiarities are most pronounced. The first range is from room temperature to 50C, the second one is from 75 to 100°C and the third range is from 100 to 150°C.

In the first range, the most interesting feature is the magnetoresitance drop in $\Delta R/R = f(H)$ dependences in low fields applied parallel to the operating current (see Fig. 1b). As mentioned above, this fact can be connected with AMR effect, namely, with alignment of the magnetization vector in Permalloy layer perpendicular to operating current (and perpendicular to the auxiliary field). A tendency to such arrangement of $\mathbf{I}_S$ near $H = 0$ may be explained by two causes. The first one is the predominance of biquadratic interlayer exchange coupling over bilinear one between Co and NiFe layers resulting in perpendicular orientation of magnetic moments in adjacent layers [6, 7]. The second reason is the appearance of uniaxial anisotropy with EA directed not along the auxiliary field (as should be waited) but normal to that field (and normal to the strip length). In our opinion, the latter cause is more real one, taking into account the following facts. First, the exchange coupling parameters are relatively small at Cu spacer thickness of 2.7 nm. The role of exchange coupling is more important at lesser interlayer thicknesses (around 1 nm, i.e. near first maximum of oscillating dependence of exchange coupling) [8]. Second, when studying the Co films coated with a thin Cu layer, namely Co(2 nm)/Cu(2.7 nm), we observed the hysteresis loops which testified the existence of in-plane anisotropy with EA directed normal to the auxiliary field (Fig. 5). The shape difference of hysteresis loops measured in two directions (Fig. 5a, b) may be explained by presence of isotropic and anisotropic regions in the film. If the nature of such anisotropy in Co/Cu system is connected with stresses, we may suppose that in NiFe/Cu/Co/Cu nanostructures the stresses arise, too. Respectively, the anisotropy in Permalloy layer in unexpected direction will be possible. This circumstance influences the peculiarities of AMR effect in the nanostructures under study.

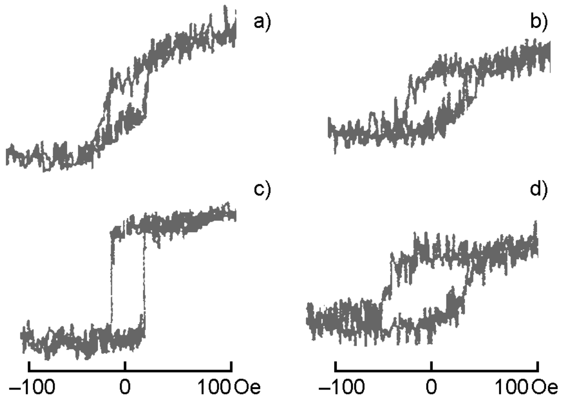

Fig. 5. Hysteresis loops of Co films coated with thin Cu layer measured along (a) and normal (b) to auxiliary magnetic field, respectively; transformation of these hysteresis loops after annealing at 100°C (c), (d).

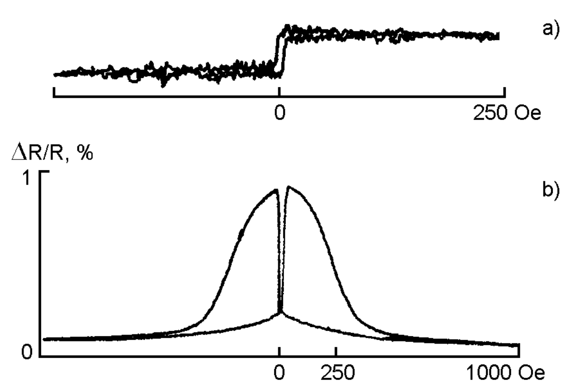

Fig. 6. Hysteresis loop (a) and field dependence of magnetoresistance (b) of NiFe/Cu/Co/Cu nanostructure after annealing at 150°C.

The additional experiments on annealing of Co/Cu and NiFe/Cu systems confirm the critical role of anisotropy. The hysteresis loops of Co/Cu system after annealing at 75–100°C were transformed and became identical in two directions. This means that the in-plane anisotropy deterioration occurs (Fig. 5c, d). But hysteresis loops of NiFe/Cu system did not change in this temperature interval (and even under up to 150°C annealing). The annealing conditions being the same, the gradual disappearing of resistance drop part of $\Delta R/R = f(H)$ curves was observed in the nanostructures under study. So we concluded that it is just the processes in Co/Cu system that play the dominant role and define the whole nanostructure features.

In the third temperature range (100–125°C), the processes causing appearance of regions with high coercive force predominate in Co layer. A rise of coercive force may be connected with occurrence of additional barriers for domain wall displacement. The grain boundaries filled with nonmagnetic materials (for example, with diffusing Cu or oxides of metals) may act as such barriers. Provided that the length of such boundaries increases and grain sizes decrease, the single-domain and even superparamagnetic particles may be generated. In this connection, the character of magnetization reversal should change from domain wall displacement to magnetization rotation for single-domain granules and further to the process described by Langevin function for superparamagnetic particles. We have measured the mean magnetization of nanostructure in H = 250 Oe at various annealing stages and compared these data with values obtained from fitted hysteresis loops for nanostructures consisting of layers with different character of magnetization reversal. A good agreement of experimental 125°C annealing data and fitted ones was obtained if we take the fitting parameters for NiFe layer the same as in as-prepared state and for Co layer, as follows: H_C = 80 Oe, s = 0.5, t = 2 nm, I_S = 400 G. It is seen that the coercive force of Co layer exceeds by 15 times that in the as-prepared state. To get the experimental mean magnetization value of nanostructure (500–550 G), the magnetization of Co layer should be about halved. After 150°C annealing, the high coercive part in hysteresis loop is not revealed in essence (Fig. 6). The mean magnetization value of nanostructure is provided with only NiFe layer contribution (Fig. 4). However, this is not always evidences the disappearance of Co as a magnetic material (for example, due to oxidation), because the GMR effect is observed in these nanostructures as before. This is possible if a larger part of Co film volume is in superparamagnetic (SP) state. In magnetic field H = 250 Oe, the SP phase contributes only a little to the total magnetization. However, the GMR effect may arise both in new granular superparamagnetic structure formed from Co and Cu and due to neighborhood of this structure with Permalloy layer.

Although the magnetic and magnetoresistive data allow to imagine the sequence of magnetic state changes during annealing, the question about motive forces of these processes is still under discussion. As our investigations have shown, the main processes should take place in upper Co/Cu layers of the nanostructure. In [9], the evolution of magnetic properties (in particular, magnetic anisotropy) with time was observed in ultrathin Co/Cu systems obtained in UHV chamber (10–8 Pa pressure). The authors explained this phenomenon by absorption and desorption of minute quantities of residual gases. We dealt with the nanostructures prepared by sputtering in Ar atmosphere after preliminary pumping down to 10^{-4} Pa. Therefore, the amount of gas included in our films may be greater than in [9]. It is possible to assume that after extraction of the samples from the vacuum chamber, the irreversible gas output onto the surface occurs. The processes are very active in upper surface layers which are enriched in vacancies. As a result, the ways for fast diffusion of atoms are formed even in such systems where solubility of components is low (as in Co–Cu system [10]). These processes lead to structure changes both in the volume of layers and on interfaces and, respectively, cause the evolution of magnetic and magnetoresistive characteristics.

To avoid the above-mentioned processes in Co/Cu layers and to improve the properties stability, we have modified the system configuration. We have deposited onto the substrate at first the Co/Cu bilayer and then the NiFe/Cu one. In fact, the stability of such nanostructures was improved noticeably. The changes of magnetoresistive properties of substrate/Co/Cu/NiFe/Cu system appear only after 150°C annealing. After ageing at room temperature during one year, the properties remained constant. Thus, we may recommend this method to improve the stability of nanostructures made up of layers with thickness smaller than 1–2 nm.

To conclude, the stability of magnetic and magnetoresistive properties of sputtered $Ni_{80}Fe_{20}$(4–6 nm)/Cu(t_{Cu})/Co(2 nm)/Cu(2.7 nm) spin-valve nanostructures has been investigated at room temperature ageing and at annealing in the range of moderate temperature from 75 to 150°C. A gradual increase of magnetoresistive ratio $(\Delta R/R)_{max}$ (up to 2 %) and transformations in field dependences of magnetoresistance $\Delta R/R = f(H)$ pronounced especially in expansion of hysteresis region, in rising of saturation field and increasing of magnetoresistance maximum H_m field have been revealed. In parallel, the changes of magnetic properties such as characteristics of hysteresis loops and mean magnetization have been monitored for nanostructures under investigation as well as for Co/Cu and NiFe/Cu bilayers. It has been shown that evolution of magnetic properties of the nanostructure as a whole are due mainly to changes in the upper Co/Cu layer properties. Basing on comparative analysis of the changes in magnetoresistive properties and magnetic characteristics, we explain the observed effects by the anisotropy destruction and an appearance of some number of separated single-domain and superparamagnetic particles in the upper Co/Cu layer. We suppose that such separation of magnetic particles may be due to gas inclusion rearrangement and an appearance of fast diffusion paths for Cu atoms. This assumption requires further investigations using the structural methods.

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Еволюція магнітних та магніторезистивних властивостей наноструктур NiFe/Cu/Co/Cu, виготовлених іонно-плазмовим розпорошенням, у процесі витримки у часі та відпалу

С.Т.Рощенко, І.Г.Шипкова, Ю.І.Чекригіна

Досліджено магнітні та магніторезистивні властивості наноструктур $Ni_{80}Fe_{20}$(4–6 nm)/Cu(2–10 nm)/Co(2 nm)/Cu(2 nm), виготовлених методом іонно-плазмового розпорошення, після витримки у часі при кімнатній температурі та відпалу в інтервалі температур 75–150°C. Досліджено магнітні властивості бішарів Co/Cu та NiFe/Cu. Проведено аналіз трансформацій польових залежностей магнітоопору та петель гістерезису наноструктур. Запропоновано пояснення еволюції характеристик всієї наноструктури як результат зміни магнітних властивостей верхнього шару Co/Cu, а саме, руйнування в ньому магнітної анізотропії, а також появою ізольованих однодоменних та суперпарамагнітних частинок.