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Formation of the Granular (Cu, Co) Alloys with Uniform Distribution of Magnetic Granules Using Co Nanoparticle Arrays

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Arrays of fcc-Co nanoparticles (NP) on amorphous polyimide and Si_3N_4/Si substrates are produced by thermal dispersion of thin metal films. The influence of the substrate material, effective thickness of the initial metal film and heat treatment on the morphology of arrays of NP has been studied. Phase transition processes during formation of structures such as magnetic Co granules in nonmagnetic Cu matrix were investigated. The possibility of obtaining by proposed method of granular (Cu, Co) alloys with a uniform distribution of Co granules in (Cu, Co) solid solution matrix was shown. Magneto-optical properties of the obtained structures were studied.

Keywords: Dispersing, Nanoparticle array, MOKE, Granular alloy.

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1. INTRODUCTION

A great attention to the study of the magnetic properties and phase transformations in film systems based on Co and Cu was induced, first of all, by the observation there of the giant magnetoresistance effect, which is widely used in electronics and sensor technology [1, 2]. Currently, the phase formation processes in both multilayer Co/Cu films and their two-component granular alloys based on Co and Cu are studied in detail. Thus, for example, the authors of the work [3] present the results obtained by different authors concerning the investigations of the phase formation processes in thin two-layer films based on Co and Cu. It is shown that formation of solid solution there occurs on the stage of condensation. Thermal treatment of the films at the annealing temperature of $T_{ann} = 900$ K leads to the formation of granular alloy which consists of the fcc-Co and hcp-Co granules in matrix of (Cu, Co) solid solution. Transition from multilayer to granular films based on Co and Cu at the decrease in the layer thickness was studied in the work [4]. Phase formation in multilayer Co/Cu films was investigated in [5]. The authors have observed the formation of meta-stable Co-Cu phase and Co clusters in the films. In this case, size of Co granules increased with the increase in the thickness of Co sublayers.

Having analyzed the publications, one can conclude that in the general case granular alloys based on Co and Cu are produced by layer-by-layer or simultaneous condensation of the components with further thermal treatment of the obtained systems. Such approach has some disadvantages. Co granules formed by such method are distributed in a random way in matrix of solid solution, and it is very difficult to control their shape and size. Moreover, it is rather complicated to exactly determine the phase composition of the obtained structures.

The approach, in which formation of the array of magnetic Co NP and non-magnetic Cu matrix is realized separately, can be an alternative to the mentioned one. Such technique was approbated in [6], where the separately formed magnetic Co clusters were deposited on the substrate simultaneously with the condensation of copper matrix. The process of formation of Co NP in Cu matrix by the sol-gel method is described in [7].

In the present work we present the results concerning the production technique of Co NP arrays on different substrate types by the method of thermal dispersion of thin metal films. The possibility of use of NP arrays for the formation of granular (Cu, Co) alloys with the uniform distribution of granules in the films is shown. Magneto-optical properties of the samples on all stages of the formation are studied.

2. INVESTIGATION TECHNIQUE

NP arrays were obtained by the vacuum annealing of thin Co films on polyimide and amorphous Si_3N_4/Si substrates. Metal Co and Cu films were deposited in a vacuum chamber of the plant VUP-5M (pressure of the residual gases 10^{-3} Pa) by the thermal evaporation, and the control of their effective thickness was carried out by the method of quartz resonator. Deposition rate was equal to 0,1-0,2 nm/c and 0,3-0,5 nm/s for Co and Cu films, respectively. Effective thickness of the obtained Co layers was 1-3,5 nm. Polyimide films-substrates were obtained from the solution of polyimide acid on copper microscopic grids with the cell size of 100 μm. The technique of substrate production is described more detailed in the works [8, 9].

Investigation of the morphology and phase composition of the samples on polyimide were performed using the transmission electron microscope PEM-125K, and statistical analysis of their morphology was realized by a specially developed software [10]. Morphology of NP arrays on Si_3N_4/Si substrates was studied by the atomic-force microscope Bruker Dimension Edge in the semi-contact mode.

Study of the magnetic properties of the samples was carried out by the magneto-optical Kerr effect (MOKE) method in the longitudinal measurement geometry at different turn angles of the sample.

3. RESULTS AND DISCUSSION

3.1 Arrays of Co nanoparticles on polyimide substrate

Investigations of the phase composition of thin Co films on polyimide substrates performed by using the

transmission electron microscopy have shown that all samples before annealing had a highly dispersed structure and consisted of the hexagonal close-packed (hcp) Co phase. Rings from the face-centered cubic (fcc) CoO phase were also present on the diffraction patterns. The typical micrograph and diffraction pattern of the freshly condensed Co film with the effective thickness of 1,5 nm are shown in Fig. 1a.

To retrace the kinetics of the dispersion process of thin-film Co, samples were isothermally annealed during different time intervals. The first stage of the formation of NP arrays is the loss of uniformity and transition from the film to island structure. As an example, in Fig. 1b we represent the micrograph and diffraction pattern from Co film with the initial effective thickness of 1,5 nm which was annealed during 30 minutes at the temperature of T_{ann} = 1000 K. The graph illustrates the formation of metal islands with linear sizes of 5-40 nm. Increase in the annealing time up to 1 hour led to the formation of arrays of metal NP and transition from the hcp-Co to the fcc-Co, about what disappearance of diffraction rings from the hcp-Co phase on the diffraction patterns imply (Fig. 1c).

It is obvious that the initial effective film thickness, thermal treatment mode, and substrate type will be the governing factors which will influence the morphology (mean radius, size distribution) of the obtained arrays of Co NP. Production of Co NP with the specified sizes is an important problem, since this fact substantially influences, in particular, the magnetic properties of NP. Thus, the authors of [11] present the dependence of the coercitivity on the diameter of Co and Fe NP at the temperature of 76 K. Its value is changed by two orders of magnetude with the particle size from 1 to 200 nm and reaches the maximum at the sizes of 10-20 nm.

An optimal interval of the initial effective thickness of Co films of 1-2 nm was chosen as the result of the performed investigations. Further increase in the thickness requires a temperature rise for the formation of NP arrays that was impossible since destruction of the substrates occurred at $T_{ann} \approx$ 1100 K.

In Fig. 2 we illustrate the micrographs and typical diffraction pattern of Co films with the initial effective thickness of 1,5 nm which were thermally treated at the temperature of T_{ann} = 870-1030 K. As the result of the analysis of the obtained images, histograms of the distribution of Co NP by size were calculated and plotted. The performed calculations indicate an insignificant increase in the mean radius r_m of metal particles from 4,4 nm (T_{ann} = 870 K) to 6,5 nm (T_{ann} = 1030 K) and decrease in their total concentration. At the decrease in the initial effective thickness of Co film from 1,5 nm to 1 nm, the value of r_m decreases from 4,5 nm to 3,5 nm (T_{ann} = 910 K), and their total concentration increases approximately two times.

It was shown earlier in the work [8] that morphology of NP arrays can be characterized by such parameters as the minimum, maximum, mean, the most probable radiuses and particle distribution by size. We have to note that the calculated value of the mean NP radius r_{calc} according to the proposed in [8] correlation at the initial effective film thickness of 1 and 1,5 nm is equal to 3,5 and 4,5 nm, respectively, and correlates well with the obtained values of r_m for Co NP. Calculated by the electron microscopy data values of the morphology parameters of Co NP arrays are given in Table 1.

In order to study the phase formation process at the formation of the structures Cu film/Co NP/polyimide, Cu films with different effective thickness were deposited on the obtained after annealing of Co films (initial effective film thickness 1,5 nm, T_{ann} = 990 K) NP arrays. Micrographs and typical diffraction pattern for the obtained samples with different atomic concentrations of Co and Cu components are illustrated in Fig. 3.

In accordance with the phase state diagram of Cu-Co system [12], system components can form a meta-stable solid solution in the whole concentration range. Results of the electron diffraction investigations of the samples imply the change in the lattice parameter of the samples with the change in the effective Cu concentration in the system (Fig. 4).

Behavior of the calculated lattice parameters and their values correspond to the Vegard rule that indicates the formation of (Cu, Co) solid solution on the stage of Cu film condensation, though the lattice parameter has lesser values than the corresponding ones for a bulk material (they are shown in Fig. 3e by the dotted line) (in contrast to the case of (Cu, Ni) system considered in [8]). Samples have rather strongly structured morphology that is confirmed by structure micrographs in Fig. 3a-d.

3.2 Arrays of Co nanoparticles on Si_3N_4/Si substrate

In order to retrace the influence of substrate material on the formation process of Co NP arrays, we have also used substrates of amorphous S_3N_4 on Si monocrystal. Deposition of thin Co films was carried out in the same conditions. Investigations of the sample morphology performed using the atomic-force microscopy have shown a considerable difference with the case of polyimide substrates. The atomic-force microscopy images of freshly condensed thin Co layers with different effective thickness represented in Fig. 5a-c indicate the formation of island structures on the condensation stage.

An annealing carried out at T_{ann} = 1100 K led to the significant change in the sample morphology. The atomic-force microscopy images of the annealed films (Fig. 5d-f) imply the formation of NP arrays. Particle sizes, as it was foreseen, increase with the increase in the initial effective thickness of Co layers and are equal to 20-40 nm, 20-70 nm, and 25-150 nm for the samples with the initial effective thickness of Co of 1,5 nm, 2,5 nm, and 3,5 nm, respectively.

Re-annealing of the samples with the initial effective thickness of 1,5 nm and 2,5 nm at T_{ann} = 1200 K (Fig. 5g,h) led to the increase in the NP sizes up to 25-50 nm and 30-80 nm, respectively. For the sample with the initial effective film thickness of 3,5 nm (Fig. 5i), a slight decrease in the NP sizes to 30-110 nm takes place. Increase in the NP size can be explained by the particle coalescence, while decrease, most probably, is connected with the change in their geometric shape in the plane of the substrate.

The profiles presented in Fig. 5j-l show the sample relief. The graphs imply a significant difference between particle sizes measured in horizontal and vertical planes. This fact, first of all, can be explained by the influence

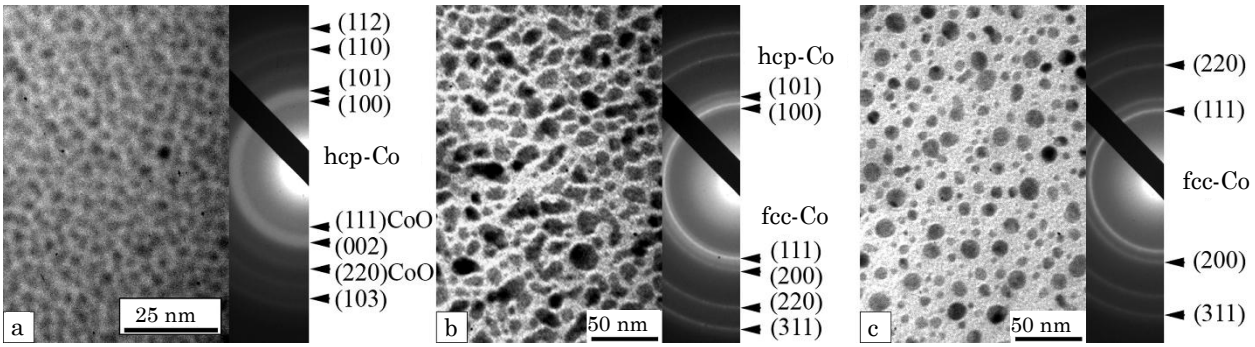

Fig. 1 – Micrographs of the structure and diffraction patterns of Co films with the initial effective thickness of 1,5 nm after deposition (a) and annealed at T_{ann} = 1000 K during 30 min (b) and 1 hour (c)

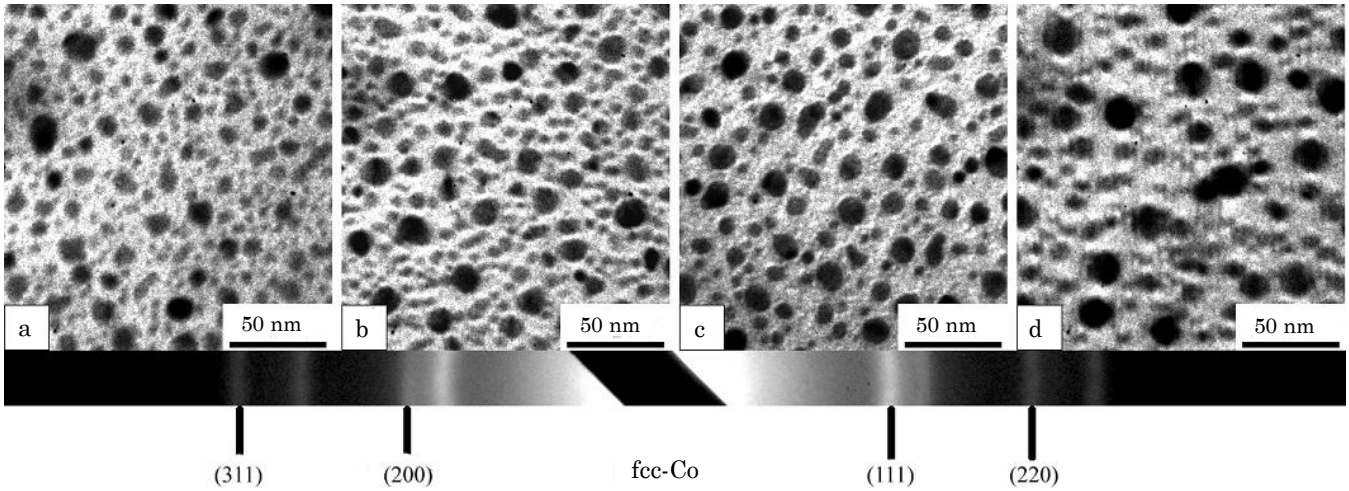

Fig. 2 – Microstructures and diffraction pattern of Co films with the initial effective thickness of 1,5 nm and annealed at the temperatures of T_{ann} = 870 K (a), 910 K (b), 990 K (c), and 1030 K (d)

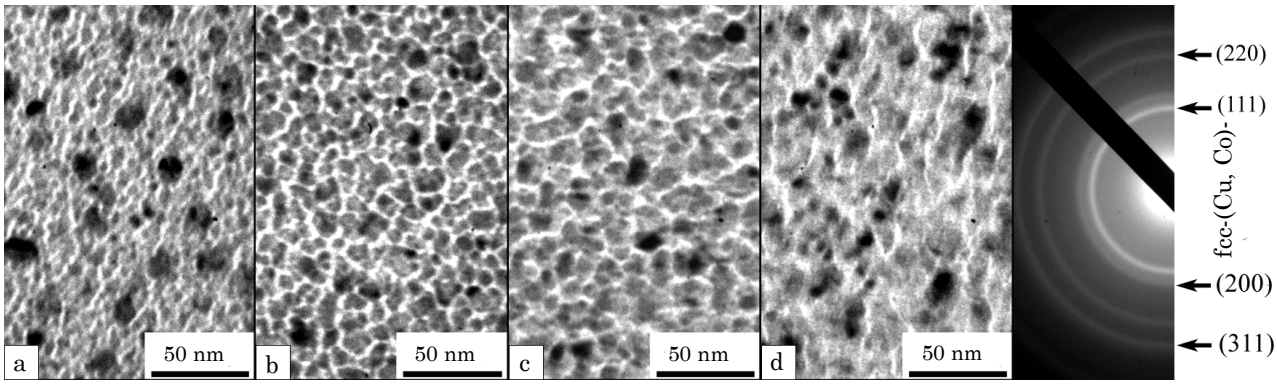

Fig. 3 – Microstructure and typical electron diffraction pattern from the obtained (Cu, Co) film alloys. Effective atomic concentration, at.% Co: 35 (a), 25 (b), 20 (c), and 15 (d)

Table 1 – Morphology parameters of Co NP arrays

Initial effective thickness of Co layer, nm	Annealing temperature, K	Maximum radius, nm	Minimum radius, nm	Mean radius, nm	Most probable radius, nm
1,5	870	8,1	1,6	4,4	2,5
1,5	890	8,2	2,0	4,5	3,5
1,5	910	9,4	2,3	5,3	4,0
1,5	990	9,5	2,5	5,7	4,4
1,5	1000	10,0	2,6	6,1	4,7
1,5	1030	10,5	2,8	6,5	5,0
1,9	970	10,0	2,1	5,7	3,5
2,1	910	9,4	2,0	5,6	4,5

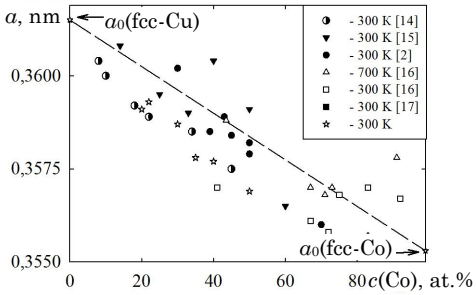

Fig. 4 – Dependence of the lattice parameter of film (Cu, Co) solid solution on the total concentration of Co atoms. Straight line corresponds to the Vegard rule

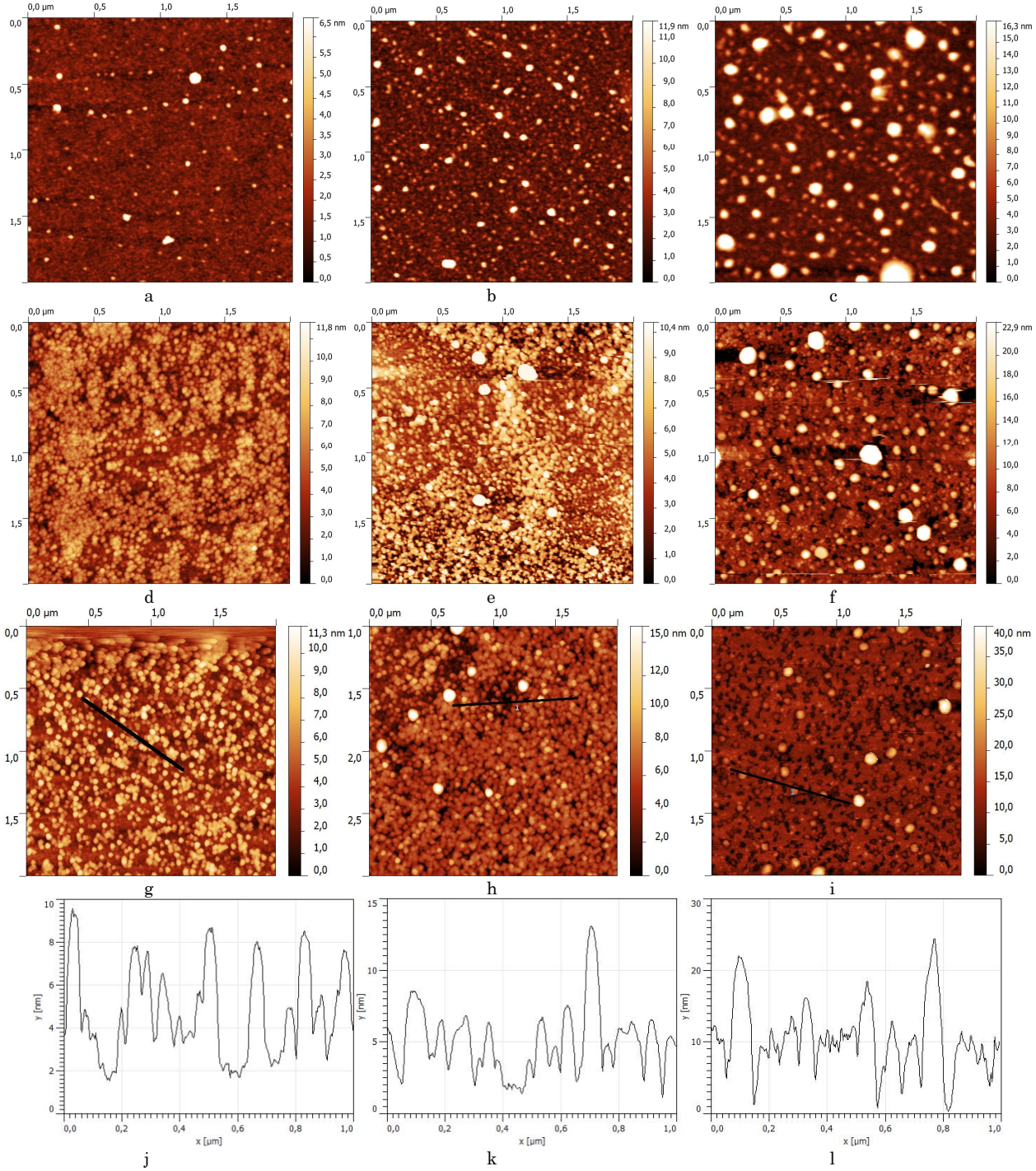

Fig. 5 – Atomic-force microscopy images of thin Co layers with the effective thickness of 1,5 (a, d, g), 2,5 (b, e, h), and 3,5 (c, f, i) nm deposited on Si_3N_4/Si substrate before (a-c) and after annealing up to T_{ann} = 1100 K (d-f) and T_{ann} = 1200 K (g-i). Graphs (j-l) correspond to the images on positions (g-i) and show the surface relief of the samples

of convolution, i.e. increase in the measured horizontal sizes of particles in comparison with the real ones due to the finite sizes of the scanning needle point of the atomic-force microscope. The authors of [13] in the study of the objects with the pre-known sizes and shape have shown a considerable influence of the convolution on the values of the measured horizontal sizes, when radius of the probe needle point becomes commensurate with the linear sizes of the studied objects. The second factor which can also partly explain a great discrepancy of the vertical and horizontal sizes of particles is their shape itself. Thus, in the work [18] using the transmission electron microscopy, the morphology and phase composition of Co NP arrays obtained by the method of dispersion of thin metal films on polyimide substrates were studied. The results presented in the works show that particle shape is more elliptical than spherical and particles are prolate in the horizontal plane.

3.3 Investigation of the magneto-resistive properties

Investigation of the magneto-optical properties of the samples on all formation stages of granular (Cu, Co) alloys on Si_3N_4/Si substrates were carried out by using the MOKE in the longitudinal measurement geometry at different turn angles of the samples. Obtained dependences for freshly condensed Co films have shown the absence of coercitivity.

MOKE measurements of the signal performed after the first annealing have shown the change in the magneto-optical properties of the samples. The obtained dependences are represented in Fig. 6a. The absence of the coercitivity for the sample with the initial effective thickness of Co layer of 1,5 nm can be explained by the superparamagnetic state of NP and orientation of the easy or hard magnetization axes. Dependences for the samples with the initial effective thickness of 2,5-3,5 nm demonstrate the appearance of a hysteresis loop, whose behavior is not changed at the sample rotating in the measurement plane.

In Fig. 6b we present the dependences of the MOKE signal measured after re-annealing of the samples at T_{ann} = 1200 K. Appearance of the coercitivity of the first sample, most probably, is explained by the increase in the NP size at annealing and transition of a part of NP to the ferromagnetic state. Though the shape of magnetic hysteresis loops obtained from the samples with the initial effective thickness of Co layer of 2,5-3,5 nm is not changed, the increase in the signal amplitude by one order of magnitude occurred.

Co NP arrays obtained after the second annealing on Si_3N_4/Si were used as the substrates at condensation of Cu films (20 nm). On top samples were covered by Au layer (3 nm) to prevent an oxidation. So, Co granules in matrix of (Cu, Co) solid solution were formed. Measurement results of the magneto-optical properties of the obtained structures are illustrated in Fig. 6c.

The dependences show that samples with the initial effective thickness of Co layer of 2,5-3,5 nm, in spite of the decrease in the MOKE signal amplitude, preserve coercitivity that, most probably, indicates the formation of the non-magnetic matrix/magnetic granules structure. Disappearance of the coercitivity for the sample with the initial effective thickness of Co layer of 1,5 nm can be explained by the formation of (Cu, Co) solid solution which has paramagnetic properties.

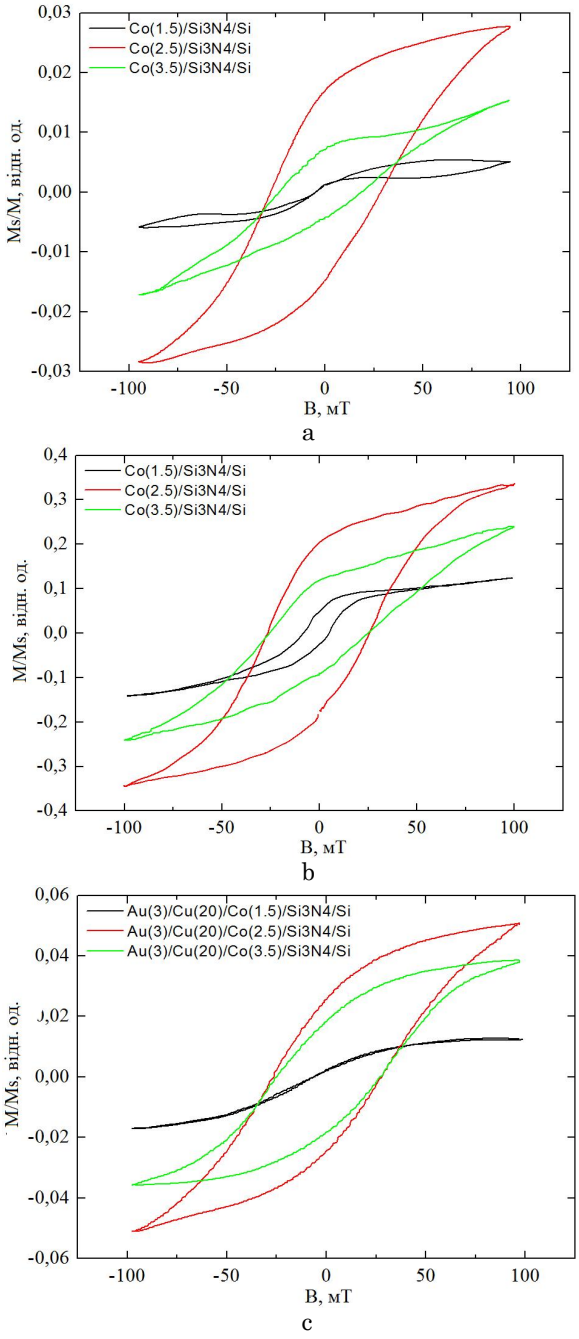

Fig. 6 – Dependences of the MOKE signal on the external magnetic field of Co films with the initial effective thickness of 1,5 -3,5 nm on Si_3N_4/Si substrates measured after the first (a) and second (b) annealing. Position (c) shows the dependences for Co NP in matrix of (Cu, Co) solid solution

4. CONCLUSIONS

Dispersion process of thin Co films during thermal annealing in vacuum allows to obtain arrays of metal NP on the surface of polyimide substrates. The mean size of particles in a greater degree depends on the initial effective thickness of Co films than on the annealing temperature. Increase in the annealing temperature leads to

the decrease in the concentration of the formed metal NP on retention of the distribution by size and insignificant increase in the particle size.

The values and behavior of the lattice parameter of the obtained structures Co NP/Cu film/polyimide subject to the effective atomic concentration of the components corresponds to the Vegard rule and implies the formation of (Cu, Co) solid solution. The performed measurements of the magneto-optical properties of two-component systems obtained on the basis of Co and Cu indicate the formation of granular (Cu, Co) alloys on Si_3N_4 substrates.

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