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Tailoring magnetic anisotropy and optical characteristics of nanostructural Co films by oblique angle deposition

© O.S. Trushin[1], I.S. Fattakhov[1], A.A. Popov[1], L.A. Mazaletsky[2,1], A.A. Lomov[3], D.M. Zakharov[3], R.A. Gaidukasov[3], A.V. Miakonkikh[3], L.A. Shendrikova[4]

[1] Valiev institute of physics and technology of RAS, Yaroslavl branch,
Yaroslavl, Russia
[2] Demidov Yaroslavl State University,
Yaroslavl, Russia
[3] Valiev institute of physics and technology of RAS,
Moscow, Russia
[4] Lomonosov Moscow State University,
Moscow, Russia
E-mail: otrushin@gmail.com

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Thin Co films on inclined Si(001) substrates were obtained by electron-beam evaporation. It has been established that at angles of incidence of the evaporated material on the substrate of more than 80° (oblique angle deposition), arrays of free-standing Co nanocolumns with a cross section of 25 nm and an aspect ratio (length/transverse size) of at least 15 are formed on the substrate surface. In this case, the magnetic easy axis of the film is oriented along the axis of the nanocolumns, which leads to the appearance of a normal component of the magnetization vector to the film surface. When the substrate rotation is turned on, an array of nanospirals is formed. With a fast rotation of the substrate (30 rpm), the magnetic easy axis approaches the normal to the film surface. At a slow substrate rotation (0.6 pm), an array of nanocoils is formed, imparting pronounced chiral properties to the film.

Keywords: nanostructuring, thin films, oblique angle deposition, chiral structures.

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1. Introduction

A promising method for the formation of thin films with special properties is their nanostructuring during growth. The formation of homogeneous and well-ordered arrays of nanostructures on the surface makes it possible to significantly change the electrical, magnetic, and optical properties of films [1]. One of the well-known technological methods that make it possible to ensure the growth of nanostructures is oblique angle deposition. This method of thin films deposition has attracted considerable interest in recent years, and many publications have been devoted to it. It is known that this method can be used to obtain nanostructures of various shapes and sizes, from inclined nanowires and nanospirals to vertical nanocolumns [2]. It has been established that the reason for the nanostructuring of films under conditions of oblique deposition is the shading effect, which consists in the fact that crystallites, which have gained a random advantage in growth at the initial stages, subsequently suppress the growth of their neighbors, intercepting the flow of atoms incident on the surface and, thereby, forming pores. One of the important functional characteristics of magnetic films is their magnetic anisotropy. Magnetic films, in which the magnetic anisotropy axis is directed at an angle to the surface, are of considerable interest for improving the technology of recording information on a hard disk [3]. In [4], the possibility of changing the magnetic anisotropy of thin cobalt films obtained by oblique deposition was demonstrated. The aim of this work was to find the optimal conditions for nanostructuring Co films on a silicon substrate under conditions of oblique angle deposition and the formation of arrays of nanocolumns with a high aspect ratio. In addition, within the framework of this work, we studied the conditions for obtaining arrays of nanospirals (nanocoils) by turning on the rotation of the substrate during growth. The creation of such nanostructures is promising for obtaining chiral films exhibiting optical activity upon reflection of light.

2. Method

A suitable technology for oblique angle deposition experiments is electron beam evaporation. This method combines a sufficiently high working vacuum and a uniform flux of material flow. A simplified scheme of the experiment is shown in Fig. 1. In this work, experiments on the deposition of cobalt films on an inclined substrate were carried out on an Oratoriya-9 electron-beam evaporation setup. The deposition conditions were as follows: base vacuum $4 \cdot 10^{-6}$ Tor; electron beam voltage 8 kV; current 0.5 A.

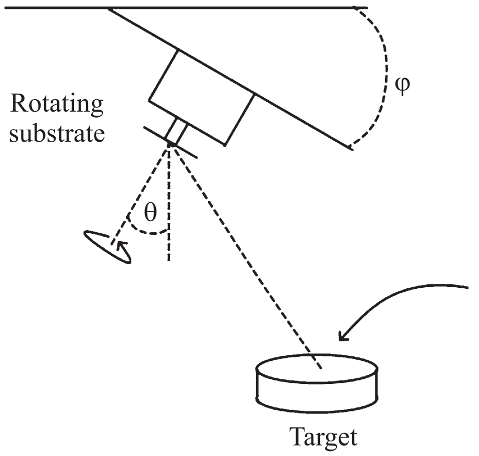

Figure 1. Schematic of the experiment for oblique angle deposition.

Cobalt films were deposited onto a rectangular substrate 20×15 mm in size, made from a standard Si(001) wafer with a thermal oxide layer 300 nm thick. The substrate was attached to the holder at an angle to the flow of the deposited material.

In addition, the holder made it possible to rotate the substrate at variable speeds. All experiments were carried out at room temperature. The film growth rate varied depending on the substrate tilt angle from 0.9 to 1.5 nm/s. The deposition time 5 min was the same for all samples.

The films as deposited were further subjected to various types of analyses. The morphology and structure of the resulting films were studied by scanning electron microscopy (SUPRA-40). X-ray diffraction analysis of the grown films was performed on a SmartLab diffractometer (Rigaku, Japan) with a rotating Cu (9 kW) anode and SBO optics (Göbel parabolic mirror). A Soller slit with an angular resolution of 0.114° was installed in front of the detector. The magnetic characteristics of the films were measured on a LakeShore vibrating sample magnetometer model 7407 (USA). The measurements were carried out at room temperature in fields up to 1.6 T. The hysteresis loops were measured at different orientations of the magnetic field relative to the plane of the samples. The optical characteristics were measured on an M-2000X spectral ellipsometer (J.A. Woollam Co, USA) at an angle of incidence of 65°, in the wavelength range of 248–1000 nm.

3. Morphology and texture of as deposited films

As a result of previous studies, it was found that the optimal conditions for nanostructuring cobalt films are realized at substrate inclination angles $\theta > 80^\circ$ [5,6]. Optimum, in this context, are the deposition conditions that provide the most pronounced nanostructuring, when the film consists of individual nanofibers separated by pores.

Figure 2 shows SEM images of a cleavage of the film structure and a top view of its surface obtained by electron microscopy. This sample of the film was obtained without turning on the substrate rotation.

As can be seen from the above figures, under these conditions, an array of nanocolumns is formed with fiber inclination angle of 60°. Each nanocolumn has transverse dimensions less than 30 nm and a length of about 400 nm.

The pattern of growth will change greatly if the same angle of inclination of the substrate is left, but we begin to change its orientation with respect to the matter flow incident on it. For this, the rotation of the substrate was included. Film growth patterns at different substrate rotation rates and tilt angle $\theta = 85^\circ$. can be seen on the SEM images shown in Fig. 3.

As can be seen from the analysis of these figures, when the substrate rotation is switched on, an array of nanospirals (helicons) is formed during film growth. When the rotation rate changes, the spiral pitch and its radius change. At a speed of 0.6 rpm, the helix pitch is about 250 nm and a radius of about 150 nm; at a rate of 1.6 rpm, the helix pitch is about 150 nm and a radius of about 100 nm; at a rate of

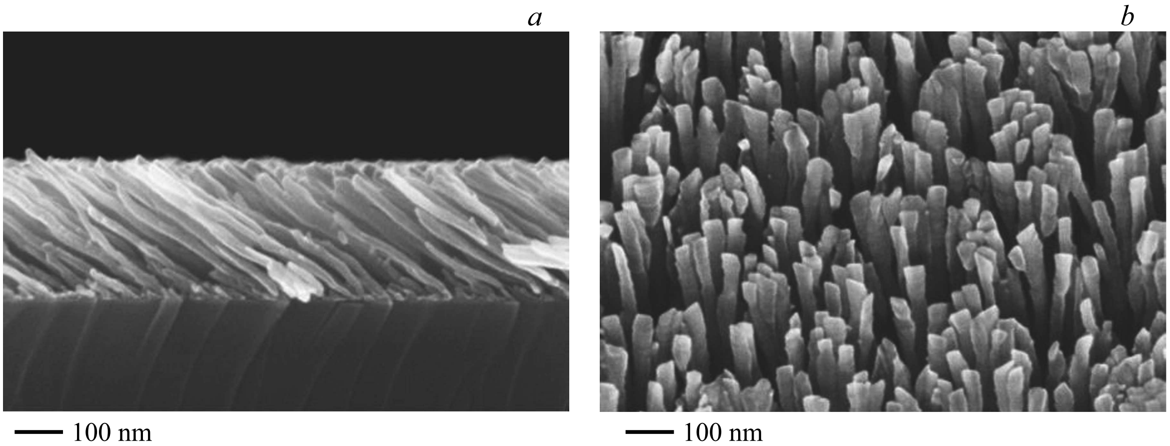

Figure 2. SEM image of a cross section of a Co film (*a*) and a top view of its surface (*b*), obtained by deposition at an angle of $\theta = 85^\circ$ without rotation.

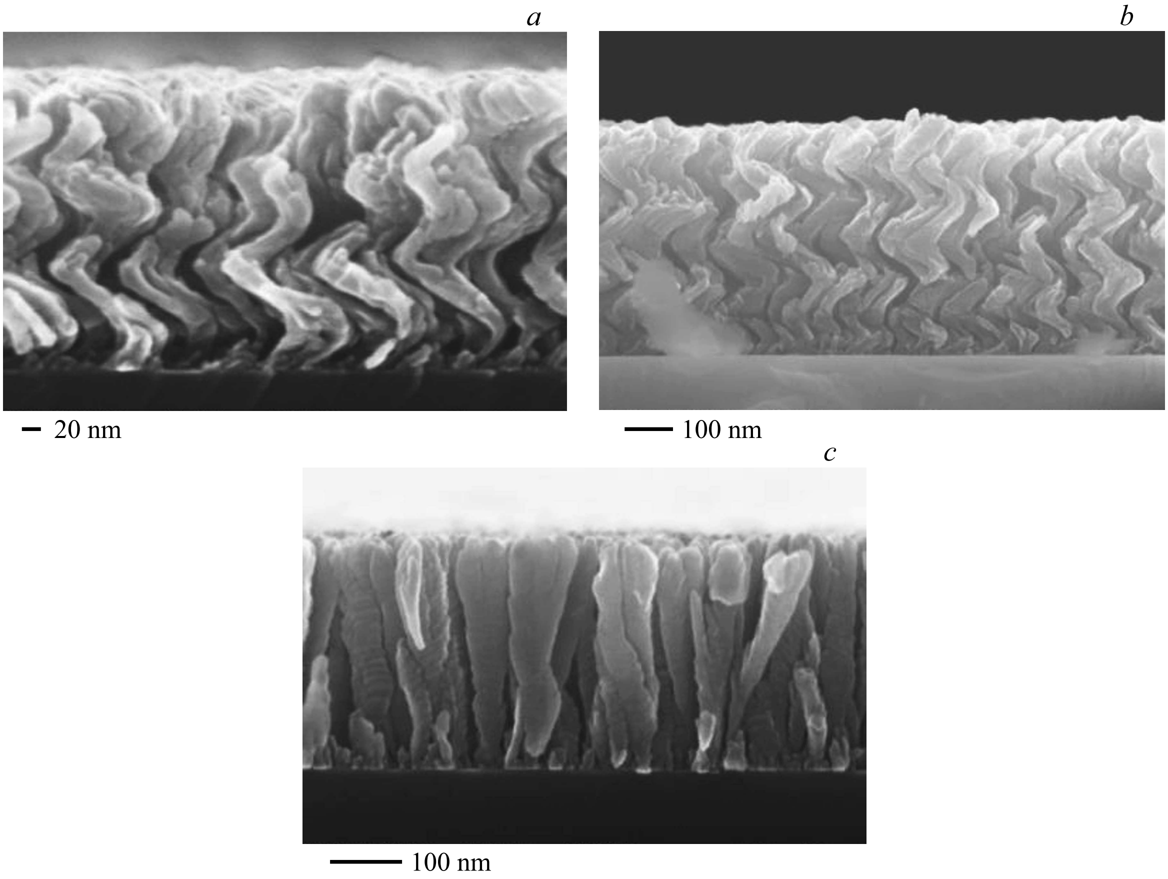

Figure 3. SEM images of cross sections of Co films obtained by deposition at an angle of $\theta = 85^\circ$ with different substrate rotation speeds: *a*) 0.6 rpm, *b*) 1.6 rpm, *c*) 30 rpm.

30 rpm, the helix pitch is practically indistinguishable. As can be seen from Fig. 3, *c*, at high rotation speeds, almost vertical nanocolumns are formed with broadening towards the top.

Thus, these experiments show the possibility of effectively controlling the growth texture by changing the deposition conditions.

4. Structural features of films

As deposited films were studied by X-ray diffraction analysis. Figure 4 shows the diffraction patterns obtained in symmetrical geometry ($2\theta/\omega$-scanning) (curve *a*) and at a grazing angle of incidence of 0.5° of the X-ray beam on the sample surface (2θ-scanning) (curve *b*).

The angular position of the diffraction maxima in both diffraction patterns from a cobalt film with nanospirals (SEM image of this sample is shown in Fig. 3, *c*) corresponds to the hexagonal phase of cobalt with the crystal lattice parameters, $a = b = 0.2505$ nm, $c = 0.407$ nm (card number PDXL 01-077-7453). At the same time, the intensity ratio of the observed three characteristic maxima 100, 002, and 101 differs markedly from the intensity ratio for the scattering model from highly disordered crystallites or „powder“. The most intense maximum 002 in the diffraction pattern (*a*) (Fig. 4) from a film with nanospirals is ~ 10 times higher than the intensity of reflections 100 and 101, in contrast to the ICDS database, where the intensity of reflection 101 is 100% against reflections 100 (26.5%)

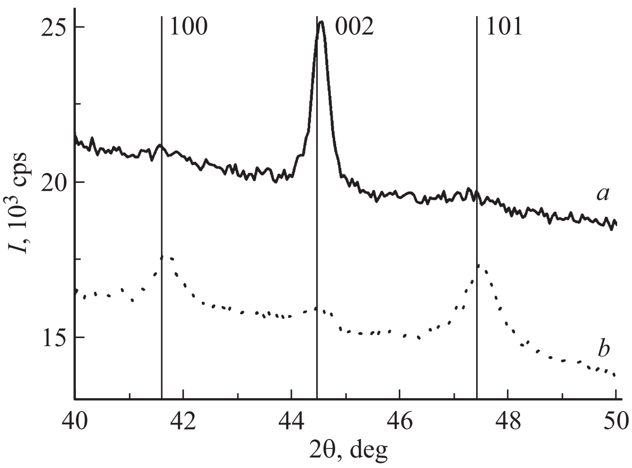

Figure 4. XRD patterns of a cobalt film with nanocoils on a Si(001) substrate grown at 30 rpm: in symmetric geometry (*a*) and at a fixed glancing angle $\varphi = 0.5^\circ$ (*b*).

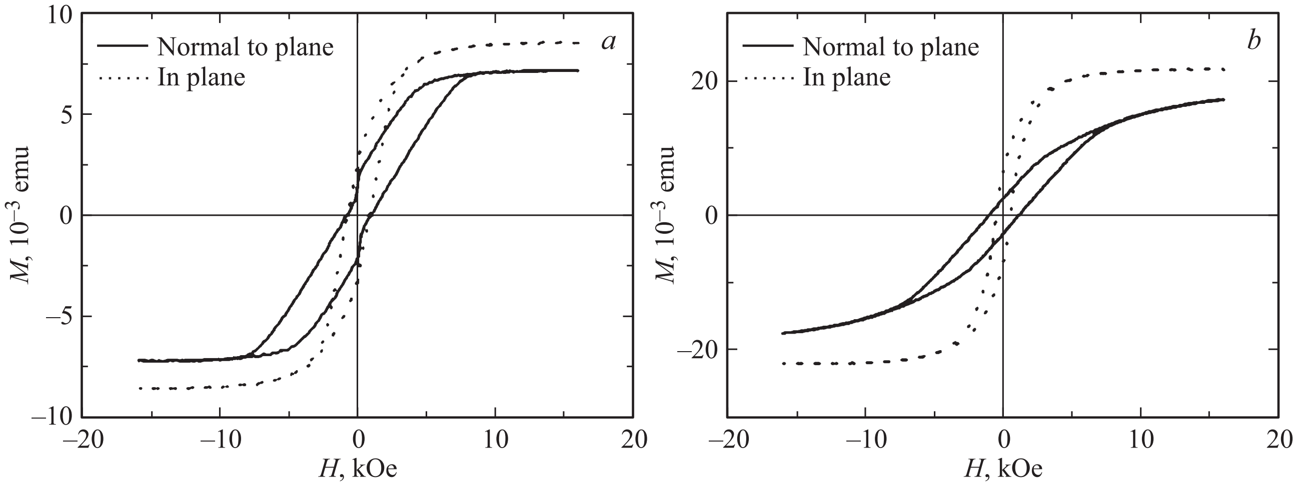

Figure 5. Curves of magnetization reversal for two samples of nanostructured films: *a*) nanocoils (rotation speed 30 rpm), *b*) inclined nanofibers (without rotation).

and 002 (27.8%). This result indicates the presence of a pronounced texture in the [001] direction in the film with nanocoils. To confirm this conclusion, let us consider the diffraction pattern (*b*) obtained with a grazing incidence of an X-ray beam on a sample. It shows that the intensity of the 002 maximum decreased to 20% against the 101 maximum.

Thus, X-ray diffraction studies showed the presence in the films of a hexagonal cobalt phase with a pronounced texture in the [001] direction.

5. Magnetic anisotropy

As shown above, the nanostructuring of cobalt films, in the absence of rotation, leads to the formation of arrays of inclined nanofibers with a high aspect ratio. It is known that nanosized magnetic fibers are characterized by an easy magnetization axis directed along the generatrix. This is due to the shape anisotropy effect. It can be expected that for films consisting of arrays of such nanofibers, the easy axis will also be oriented along the fibers.

Our measurements of the magnetic characteristics of these films confirmed the previously discovered [4] tendency for the orientation of the easy magnetization axis to change with increasing substrate tilt angle. At large tilt angles, it is oriented along the axis of the nanofibers, thereby ensuring the inclination of the magnetization vector to the film surface.

For magnetic recording media, the perpendicular orientation of the easy axis of magnetic anisotropy is optimal. To do this, it is necessary to orient the nanofibers perpendicular to the substrate. As shown above, one of the ways to achieve this result is to increase the substrate rotation rate during growth. Under these conditions, nanocoils with a very small pitch are formed (Fig. 3, *c*).

With this in mind, comparative measurements of the magnetization reversal curves of films consisting of vertical nanocoils and inclined nanofibers were carried out. The measurements were carried out on a vibrating sample magnetometer (VSM). For each sample, several measurements of the magnetization reversal curves were carried out for different orientations of the external magnetic field: perpendicular to the film plane and along the film plane for two orientations of the sample. Typical results are shown in Figure 5.

As can be seen from the above dependences, vertically standing nanohelices (nanocolumns) are characterized by the orientation of the easy axis closer to the normal. This is evidenced by the beginning of the formation of a step in the region of low fields on the hysteresis loop (solid curve in Fig. 5, *a*) and reaching saturation. However, to improve the functional characteristics (achieving a distinctly pronounced perpendicular magnetic anisotropy), further work is required to optimize the technology.

Thus, the experiments performed showed that, by changing the technological conditions of deposition, it is possible to control the direction of the magnetic anisotropy of the film.

6. Optical characteristics

As we saw earlier, when the substrate rotation is turned on during film growth, an array of nanospirals is formed. All these nanocoils are twisted in the same direction, which is determined by the direction of rotation of the sample. This growth morphology leads to symmetry breaking in the film plane with respect to specular reflections. This property is called chirality. Based on general symmetry considerations, it can be expected that the chirality of a surface can manifest itself in optical reflection phenomena, since a light wave can have circular polarization. Under certain conditions, light

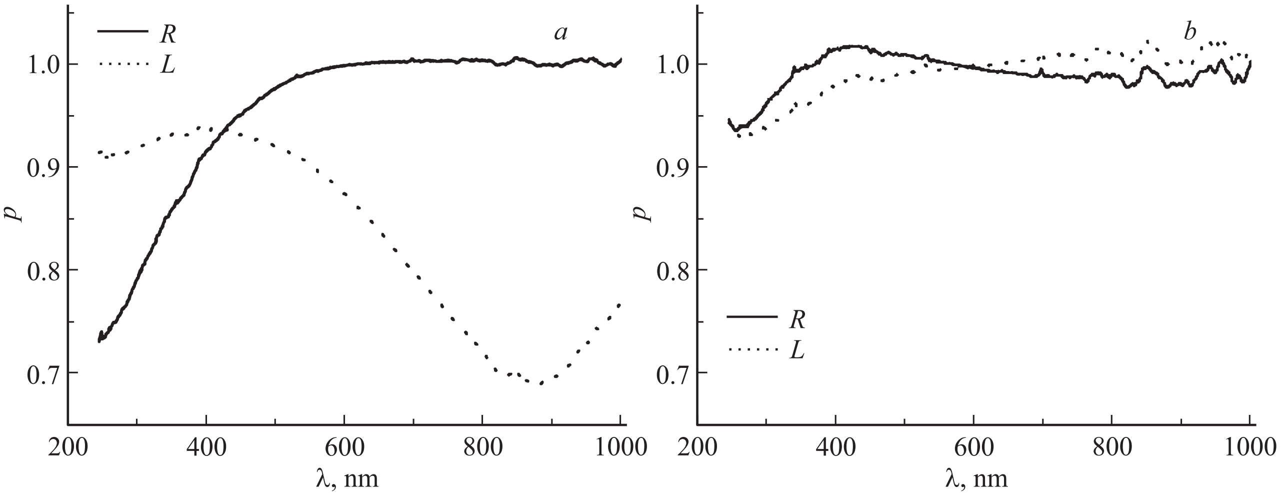

Figure 6. Dependence of the degree of polarization of the reflected wave on the wavelength of the radiation used for two types of incident circularly polarized waves (right-R and left-L): a) for a sample with a rotation of 0.6 rpm, b) for a sample with a rotation of 1.6 rpm.

having, for example, right circular polarization will interact differently with nanospirals twisted to the right and to the left. Therefore, it is reasonable to assume that this effect will manifest itself when circularly polarized light is reflected from a chiral surface. In this case, it can be expected that the geometric dimensions of the nanohelix (the pitch and its radius) should affect the polarization properties of the structure. To test these assumptions, ellipsometric studies of the obtained samples were carried out. An M-2000X spectral ellipsometer (J.A. Woollam Co, USA) was used. For each sample, complex measurements of the Stokes vectors were carried out in the wavelength range of 248–1000 nm at an angle of incidence (and reflection) equal to 65°. As a result, the elements of the Muller matrix were calculated [7]. These data were used to analyze the polarization properties of the resulting structures. The above assumptions are fully confirmed by the obtained experimental data.

Figure 6 shows the dependences of the degree of polarization of the reflected radiation for two types of the incident circularly polarized waves (right and left) on the wavelength for two different samples obtained at different rotation speeds.

As can be seen from the analysis of Fig. 6, a, the degree of polarization changes differently with a change in the wavelength for the right and left polarizations for the sample obtained at the slowest rotation speed (0.6 rpm). Apparently, this fact can be understood by comparing the wavelength and geometric dimensions of the nanospiral (helix pitch and radius). For this sample, as can be seen from Fig. 3, a (SEM image), the helix pitch is about 250 nm, which is comparable to the wavelength of the radiation used in the measurements. It is in the region of short wavelengths that a significant depolarization occurs (a decrease in the degree of polarization by 30%) of one of the types of the circular wave (R). On the other hand, for another type of polarization (L), a decrease in the degree of polarization takes place in the region of longer wavelengths (900 nm). This can occur due to a phase failure during reflection or absorption of light by metal nanostructures. On the other hand, for the sample obtained at a higher rotation speed (1.6 rpm), the dependences of the degree of polarization on the wavelength for the two types of polarization differ little. For this sample, the helix pitch and radius are smaller and the depolarization effect is less pronounced. Thus, by varying the sample rotation rate during growth, it is possible to change the polarization properties of the resulting film.

7. Conclusions

Thus, as a result of the experiments, it was found that at large angles of inclination of the substrate (more than 70°), nanostructuring of the cobalt film occurs. The optimal conditions for nanostructuring (when the nanostrips are distinctly separated) are achieved at a substrate tilt angle of 85°. In this case, an inclined fibrous structure with fiber sizes up to 30 nm is formed. Our measurements of the magnetic characteristics of these films confirmed the tendency for the orientation of the easy magnetization axis to change with increasing substrate tilt angle. At large tilt angles, it is oriented along the axis of the nanofibers, thereby ensuring the inclination of the magnetization vector to the film surface. When the substrate rotation is turned on, an array of nanospirals is formed. By varying the substrate rotation rate, it is possible to obtain nanospirals with different geometric dimensions (helix pitch, spiral radius). It should be noted that all nanohelices are twisted in the same direction, which imparts chirality properties to the film. This, in particular, leads to an asymmetry of the optical characteristics upon reflection of right- and left-hand circularly polarized light. This morphology can be promising for application in the field of nanosensorics and nanocatalysis, as well as for the creation of optically active surfaces and as a medium for high-density magnetic recording of information.

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Conflict of interest

The authors declare that they have no conflict of interest.

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