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Chiral metasurfaces based on arrays of Co nanospirals obtained by glancing angle deposition

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The results of experimental studies of chiral film structures based on arrays of cobalt nanospirals obtained by glancing angle deposition are presented. It is shown that under conditions of electron beam evaporation, an array of nanospirals twisted in one direction is formed on a rotating inclined substrate. By changing the rotation speed of the substrate, the geometric dimensions of the nanospirals (spiral pitch, spiral radius) can be changed. The chiral metasurface obtained in this way demonstrates a pronounced asymmetry of optical characteristics in light reflection with respect to the right and left circular polarization. The experimental results confirm the dependence of these effects on the chirality signs of the obtained samples (that is, on the direction of twisting of the nanospirals).

Keywords: nanostructured, thin films, glancing angle deposition, chiral metamaterials, circular dichroism.

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1. Introduction

The process of light interaction with nanostructured thin films is of high interest for both, the fundamental science (to study the fundamental mechanisms of light interaction with a substance), and for possible practical applications (for development of polarizers, selective filters and optical sensors). In particular, the nanostructured films, which are the ordered arrays of nanospirals, are an example of chiral metamaterials widely discussed today in the literature [1–4].

Such structures consist of periodically arranged single-geometry elements (meta-atoms) on a flat substrate and have typical dimensions comparable with the visible light wavelength. A distinctive feature of such elements is absence of a mirror symmetry which gives a property of chirality to such film structure. This property can be observed as various optical effects with different nature of interaction of this material with right-handed and left-handed polarization light. When incident light reflects from such a surface a change in light polarization and intensity occurs. These effects may be used in practice to create optical filters, polarizers and sensors of various kinds. Nanostructures obtained by nanolithography and nanoimprinting methods are featuring the most perfect shape and equal sizes [2,4]. However, high cost of such methods makes a wide practical application of these metamaterials unrealistic. In recent years a low-cost method of glancing angle deposition has been used to obtain the chiral metamaterials (GLAD) [5]. Within this method an array of nanospirals is obtained under electron-beam evaporation on the inclined substrate due to a shadowing effect. This effect is provided due to the fact that crystallites that accidentally have grown at initial stages of sputtering further start shadowing out the neighboring elements, thus, suppressing their growth. Thus, pores and an array of separate nanostructures form in the growing film. When the substrate starts rotation around the normal line to its surface during the elements growth it will result in gradual shift of the shadow and formation of nanospirals. At that all nanospirals are synchronically twisted in one direction which makes chiral the entire surface. By changing the substrate rotation speed it is possible to change the nanospirals geometry (helix pitch, radius and etc.) [3,6]. Moreover, by changing the direction of substrate rotation the direction of nanospirals twisting may also be changed, i.e. the sign of chirality.

Optical properties of thin film chiral metamaterials obtained by glancing angle deposition (GLAD) with substrate rotation are already well studied [1–5,7–10]. These materials are proved to have high optical activity. At that, resonances on spectral characteristics for the wavelengths corresponding to nanostructures geometry are observed. In the English-language literature this effect was called „circular Bragg phenomenon“ [9]. The chiral nanostructures are mainly fabricated from the dielectric materials due to their higher functional optical parameters (transparency, refraction index).

In this paper, cobalt chiral nanostructures are considered. When light interacts with metal nanostructures plasmon resonances may be excited, when the nanostructure geometry is consistent with the incident light wavelength. In this case, a standing wave arises in the spiral [1,10]. The theoretical analysis demonstrated that plasmon resonances in the nanospirals interact with the right-hand and left-hand polarization waves in different way [10].

Previous papers described the effects of optical asymmetry on samples with various nanospiral sizes. It was demonstrated that the degree of such effects depend on the helix pitch of the nanospiral structure [6]. Moreover, the experiments demonstrated that by changing the sputtering process conditions the film magnetic anisotropy can be controlled. It is shown that with a significant increase in the rotation speed (30 revs/min and more) of the substrate, the spiral pitch decreases and practically vertical columns with a widening towards the top are formed. In this case, the magnetic easy axis shifts toward the normal to the film surface [6].

The purpose of this paper is to demonstrate optical asymmetry when reflecting the circularly polarized emission on samples with various chirality sign (i. e. with various direction of the nanospirals involution).

2. Experimental procedure

Electron-beam evaporation is the most suitable technology for the glancing angle deposition experiments. This method combines a pretty high level of operating vacuum and homogeneous flow of the sputtered material. Simplified experimental setup is shown in Figure 1. Here, to check directly the optical asymmetry effect we used sputtering for two identical samples in similar conditions but rotating in opposite directions. Thus, in these conditions we may get various samples with different chirality sign (nanospirals have a clockwise involution (Rsample) and counter-clockwise involution (Lsample)). Cobalt films were deposited on an inclined substrate using an electron-beam evaporation installation Oratoria-9. The following sputtering conditions were provided for the films deposition: base vacuum $4 \cdot 10^{-6}$ Tor; voltage of electron beam 8 kV; current 0.5 A. The cobalt films were deposited on rectangular substrates 20 × 15 mm fabricated of standard Si(001) wafer with a layer of thermal oxide of 300 nm. Two identical substrates were mounted on holders at the same angle to the flow of the deposited material.

Moreover, the holders provided for a possibility of substrates rotation with equal speed, but in opposite directions. The films obtained in this way were then subjected to various types of analysis. The morphology and structure of obtained films was studied by scanning electron microscopy (SUPRA-40). Their optical characteristics were measured using spectral ellipsometer M-2000X (J.A. Woollam Co, USA) at an angle of incidence 65°, and in the range of wavelengths 248−1000 nm.

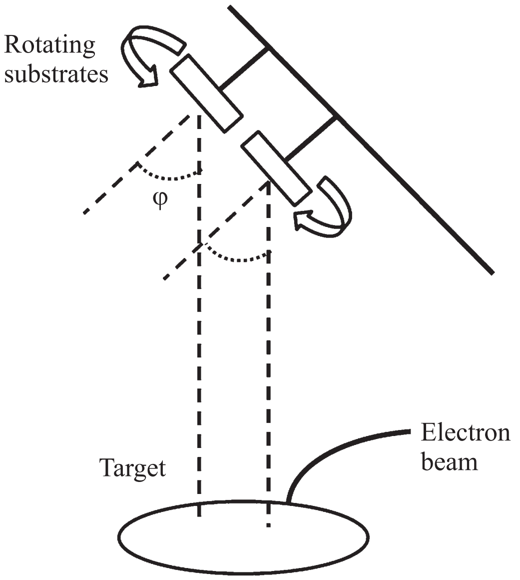

Figure 1. Experimental setup with glancing angle deposition simultaneously on two substrates rotating in opposite directions.

3. Morphology and texture of deposited films

As a result of previously conducted studies, it was established that optimal conditions for nanostructuring of cobalt films are realized at substrate tilt angles greater than 80° [6]. In this context, the optimal conditions for deposition are those that provide the most clearly expressed nanostructuring, when the film consists of individual nanofibers separated by pores. An array of tilted nanocolumns will be formed in these conditions. Angle of inclination is about 60°. Every such nano-fiber has cross-sectional dimensions of 30 nm and length of about 400 nm. The growth pattern will drastically change when keeping the same inclination angle of the substrate but changing its orientation relative to the incident flow of deposited material. For this purpose, the rotation of the substrate was enabled. The corresponding growth patterns for samples obtained under various substrate rotation speeds are given in Figure 2.

As can be seen from the analysis of these figures, when the rotation of the substrate is turned on during the film growth process, an array of nanospirals (helicons) is formed. The helical pitch changes with the change of the substrate rotation speed. At 0.6 rpm the helical pitch is about 250 nm, at 1.6 rpm it makes about 200 nm.

Thus, the experiments demonstrate a possibility of effective control of the growth texture by changing the sputtering conditions.

4. Optical characteristics

As could be seen earlier, an array of nanospirals is formed during the film growth process if the substrate

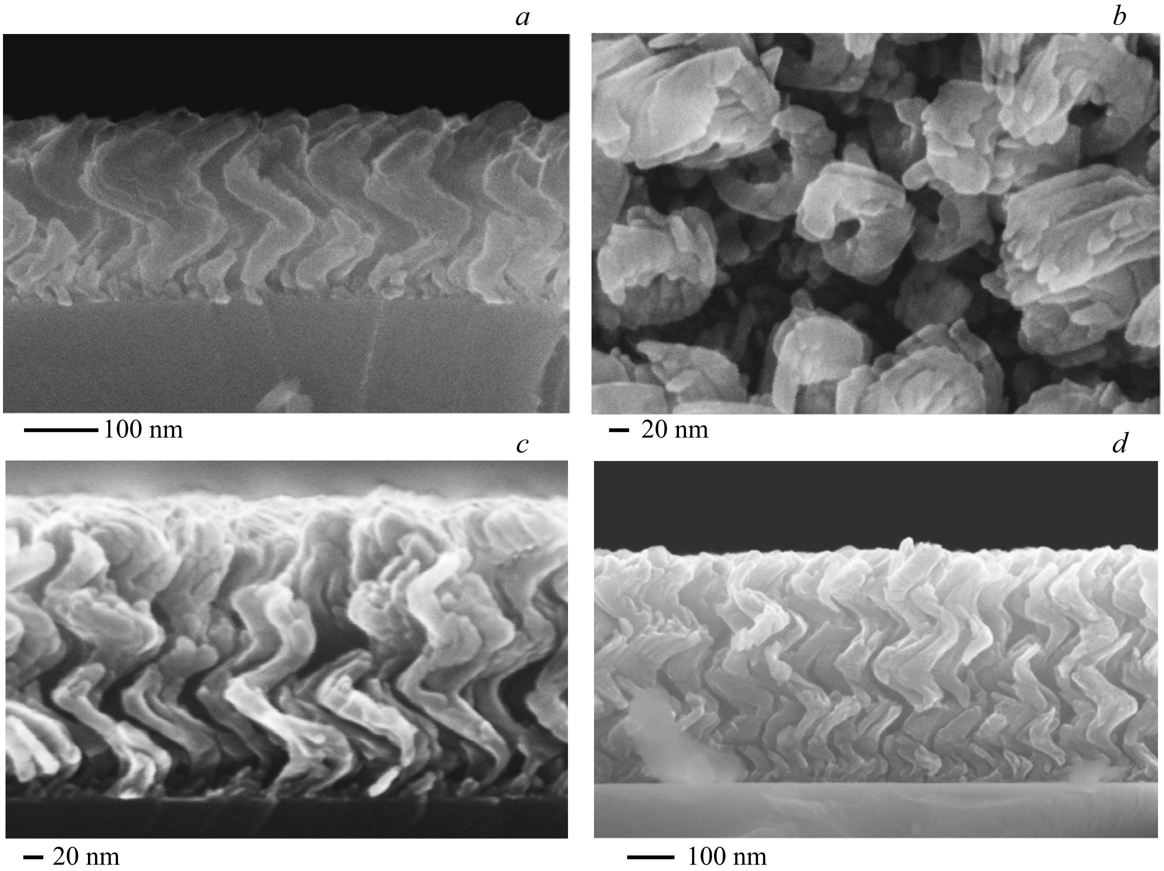

Figure 2. Microscopic images of the nanostructured Co/Si films deposited at different substrate rotation speeds: *a*) and *b*) 0.3 rpm cross-sectional cut and top view, respectively *c*) 0.6 rpm cross-sectional cut *d*) 1.6 rpm cross-sectional cut.

rotation is included in sputtering. All these nanospirals are twisted in one and the same direction associated with the sample rotation direction. Such growth morphology leads to breaking symmetry in the film plane relative to the mirror reflections. This property is called chirality. Based on general symmetry considerations it can be expected that chirality of a surface can be observed as optical effects of reflections, since the light wave can have a circular polarization. Under certain conditions the light, e. g. with a right-handed polarization, will have different kind of interaction with nanospirals with right and left involution. Therefore, it is reasonable to assume that this effect will be observed when the circularly polarized light is reflected from a chiral surface. At that, helix pitch of the nanospiral can be expected to impact the polarization properties of the structure. To check these assumptions a series of ellipsometry studies of the obtained samples were carried out. Spectral ellipsometer M-2000X (J.A. Woollam Co, USA) was used in the studies. This kind of ellipsometers are widely used for an in-situ control of the films growth [7].

Complex Stokes vectors measurements were made for each of the samples within the wavelengths 248–1000 nm at incident light angle (and reflection angle) equal 65°. Muller matrices were calculated as a result [8]. The polarization properties of obtained structures were analyzed based on these data. The above-mentioned assumptions are qualitatively confirmed by the obtained experimental data.

In most of papers describing the chiral metamaterials the measurement for through-transmission or reflection of an normally incident light are considered. In this paper an alternative method of experimental studies was used based on the reflection spectral ellipsometry data. A circularly polarized wave reaches a sample. The degree of polarization of the reflected wave was chosen as the main measured characteristic. This value is equal to the ratio of polarization component intensity to the full intensity of reflected emission. The variation of this value is due to depolarization effects. Sample light incidence angle being 65 degrees.

Figure 3 illustrates the degree of reflected light polarization for the two kinds of incident circular-polarized wave (Figure 3, *a* — right-handed and Figure 3, *b* — left-handed) for two samples obtained at rotation speed of 0.6 nm. Here we obtained solid curve for a sample with nanospirals twisted to the right (Rsample) and dotted curve for a sample with nanospirals twisted to the left (Lsample).

As we can see from this Figure the degree of polarization changes differently with the change of the wavelength for

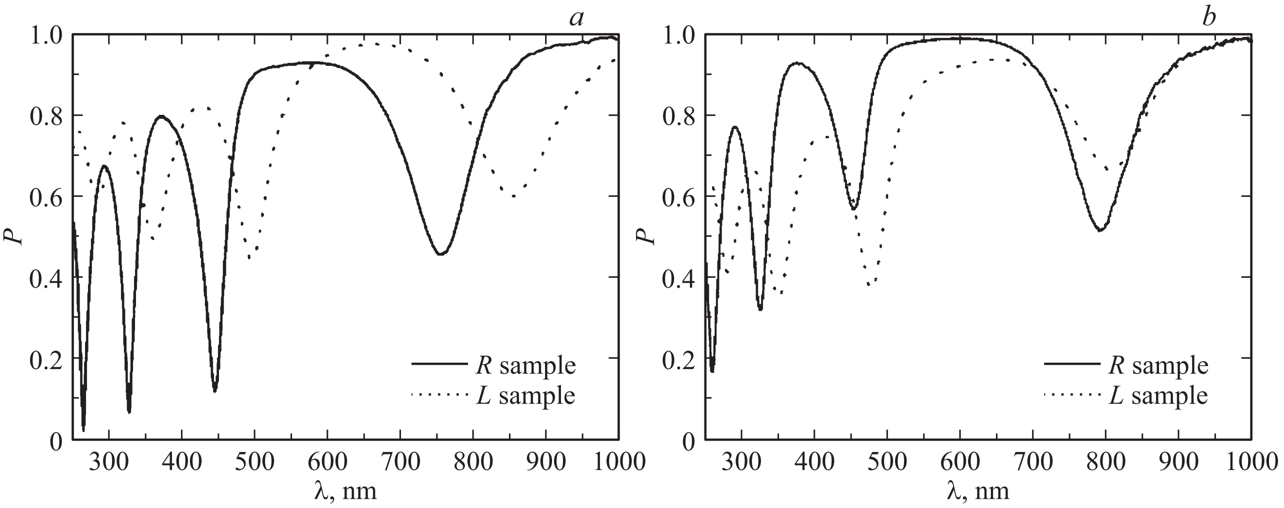

Figure 3. Reflected wave polarization degree versus emission wavelength for the two types of incident circularly polarized waves *a*) right and *b*) left for two samples with different chirality (Rsample and Lsample).

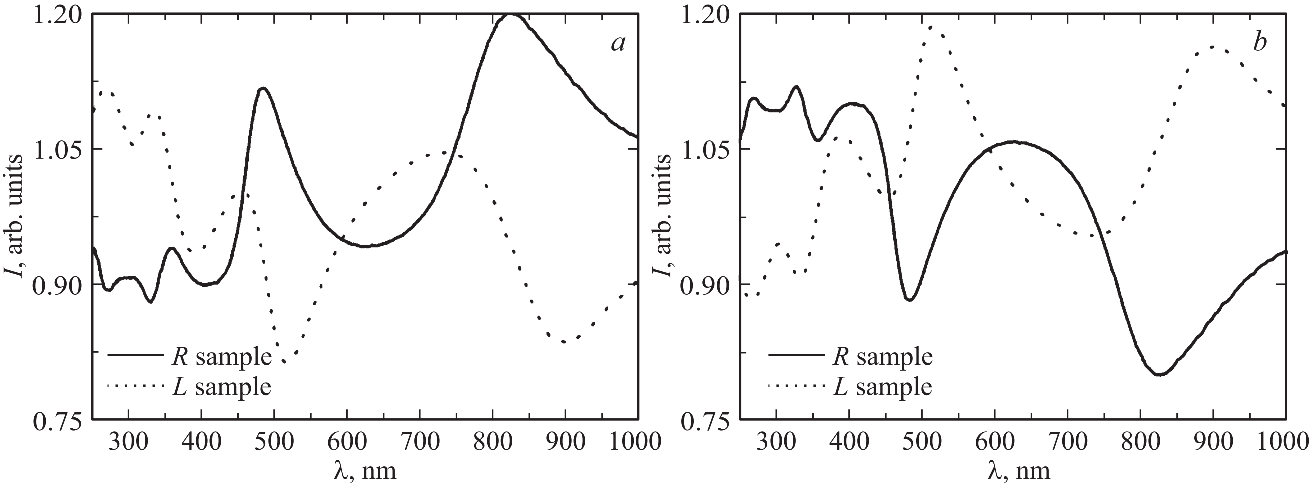

Figure 4. Reflected wave intensity versus emission wavelength for the two types of incident circularly polarized waves *a*) right-handed and *b*) left-handed for two samples with different chirality (Rsample and Lsample).

the right and left polarization and for two different samples with different chirality signs. We may understand this by comparing the wavelength and size of the nanospiral helical pitch. For this type of sample as seen from Figure 2 (SEM image) the helical pitch is about 250 nm which is comparable with the wavelength of emission used during the test. It is the area of small wavelengths where significant depolarization (reduction of polarization degree) of one of the circular wave types occur. This may be caused by a phase failure during reflection or various absorption of light by metallic nanostructures. Thus, by varying the helical pitch of the nanospiral we may control the polarization properties of the obtained film.

These observations are also proved by the curves of reflected light intensities versus wavelengths as shown in Figure 4.

By analyzing the figures we may say that the right-handed (Rsample) and left-handed (Lsample) samples reflect the light of various circular polarization differently. The nature of these differences being dependent on the incident light wavelength. These results indicate that light absorption effects are different for the light absorbed by nanospirals of different chirality (circular dichroism). These observations also prove a clearly distinct asymmetry of optical characteristics of obtained samples.

The results of measurements for samples at various substrate rotation speeds showed significant changes in their optical characteristics. At low rotation speed (0.2 revs/min) a partial helical turn is formed in the film thickness. In such a structure no any resonance plasmon excitation occurs and the polarization degree remains practically the same for both types of the circular-polarized waves. At rotation speed of 0.3 revs/min two helical turns are formed. In these conditions one of the types of circular polarization excites a plasmon in this structure which leads to wave energy absorption and depolarization (cross-polarization). The observed minima of the degree of polarization correspond to such plasmonic resonances. Ar rotation speed of 0.6 revs/min the spirals with 4 helical turns are formed. Under these conditions, plasmons are also excited, but those corresponding to other wavelengths and the positions of the minima on the curve are shifted. When the substrate rotates with a speed of 1.6 revs/min the multi-turn spirals are formed, while no conditions for resonance arise and no characteristics asymmetry is observed.

The film growth processes under these conditions are stochastic in nature, therefore the formed array of nanospirals is characterized by a significant spread in size and shape. However, a cumulative action of a large number of nanospirals causes a chiral environment effect and demonstrates a significant symmetry of optical characteristics of obtained films. When writing this article, additional studies of such films deposited on a transparent substrate were carried out in transmission geometry using the circular dichroism spectroscopy method, which confirmed the significant optical activity of these structures. To enhance the observed effects it is necessary to increase the regularity of nanospirals layout across the film area and reduce their geometry and shape scattering. To enhance the observed effects, it is necessary to increase the regularity of the arrangement of nanospirals on the film area and reduce the spread of their geometric sizes and shapes. Subject to further work on optimizing the technology and improving the functional characteristics of the resulting films, these effects can be used to create optical filters, polarizers and various optical sensors.

5. Conclusion

Thus, the studies demonstrate that at high substrate inclination angles (more than 70°) the cobalt film becomes nanostructured. If the substrate rotation is added an array of nanospirals is formed. By varying the substrate rotation speed it is possible to obtain the nanospirals with different helical pitch. It shall be emphasized that all nanospirals are synchronically twisted in one direction which makes chiral the entire surface of the film. This, in particular, leads to asymmetry of optical characteristics during reflection of the right-handed and left-handed polarization light. The results of experiment prove the dependence of these effects on the sign of chirality of obtained samples (i. e. on direction of nanospirals involution). This morphology can be perspective in terms of use in the sphere of nano-sensorics and nanocatalysis, as well as for design of polarizers and optical filters.

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Conflict of interest

The authors declare that they have no conflict of interest.

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