

УДК 517.9

Magneto-optical Properties of Nanogranular Co-Ti-O Films

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Received 10.12.2009, received in revised form 15.01.2010, accepted 11.02.2010

In this work the results of investigations of the magneto-optical properties of Co-Ti-O nanogranular films obtained under conditions of the solid-state reaction with the oxygen exchange reaction in the CoO/Ti layered structures are presented. The formation of the granular films with composition in the area of and below a percolation threshold is shown. The magneto-optical spectra features of the obtained films with the filling factor of magnetic phase from 0.3 to 0.52 in comparison with spectra of uniform metallic films are found.

Keywords: nanogranular films, solid-state reaction, synthesis, magneto-optical properties, Kerr effect.

Magnetic granular films consisting of ferromagnetic nanoclusters embedded in an insulating matrix were extensively investigated in recent years because of their giant magnetoresistance [1], giant extraordinary Hall effect [2], high magnetorefractive effect [3], magneto-optical features [3–7] and potential magnetic recording applications [8]. It is known that the magneto-optical properties of composite systems depend on the filling factor (relative volume) of magnetic fraction and properties of a dielectric matrix [9]. Most of the performed research deals with metal particles in SiO₂ and Al₂O₃ dielectric matrixes [3, 5–7]. From this point of view the magneto-optical properties of the granular films in TiO₂ matrix with the dielectric constant exceeding the dielectric constants of SiO₂ and Al₂O₃ are of interest [10].

There exist several methods of the nanogranular structures preparation. Solid state reactions in layered systems metal-dielectric or metal-semiconductor is one of the perspective methods from the viewpoint of creating nanoparticles with narrow size distribution. Earlier it has been shown that the products of solid-state reactions which are passing in layered Fe₂O₃/Al and Fe₂O₃/Ti structures with the oxygen exchange reaction in layers are Fe nanoparticles imbedded in dielectric matrixes Al₂O₃ and TiO₂, respectively [11]. In this case, the oxide matrix had a nanocrystalline or amorphous structure.

In this work the results of investigations of magneto-optical properties of Co-Ti-O nanogranular films with the filling factor $X = 0.2 - 0.52$ obtained under conditions of solid-state reaction with oxygen exchange in the CoO/Ti layered structures are presented.

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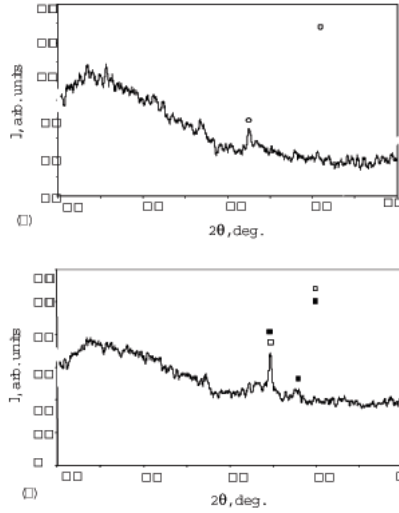


Fig. 1. X-ray diffraction pattern of the layer CoO/Ti structure (a) before and (b) after annealing

Taking into account high chemical activity of the titanium in relation to oxygen, for preparation of granular Co films in a dielectric matrix of titanium oxide we used the following reaction:



The CoO and Ti layers were reagents of reaction (1). It follows from the reaction equation (1), that the relative volume $X = V(\text{Co})/V(\text{Co} + \text{Ti-O})$ of a magnetic phase (Co) in the reaction products is 0.4. To change the ratio of volumes of the magnetic and dielectric phases in products of reaction it is necessary to change not only the ratio of the reagent layer thicknesses but also the pressure of residual gases. The film preparation with X values near 0.4 and lower seems to be easier comparing to X exceeding 0.4. In the first case cobalt reduced completely and the surplus titanium with respect to the equilibrium condition in equation (1) can be oxidized during annealing.

The CoO films were obtained by oxidation of the cobalt films in air at temperature 670 K. The cobalt films were prepared by thermal evaporation of Co metal on cover-glass plates in vacuum 10^{-6} Torr at temperature 470–520 K. The titanium layers were deposited on the CoO films by ion-plasma sputtering of a bulk titanium target in an argon atmosphere at a pressure $(4-5) \times 10^{-5}$ Torr and the substrate temperature 320 K. Thus, the samples for solid-state reaction consisted of two layers. The solid-state reaction was carried out in an isothermal annealing mode at temperature 620–670 K under a pressure $10^{-6} - 10^{-5}$ Torr. The layered structures with filling factor of magnetic phase $X = 0.2 \dots 0.52$ have been obtained.

The chemical composition and thickness of the obtained samples were defined by X-ray fluorescence analysis. The X-ray diffraction patterns were obtained with the DRON-3 diffractometer (CuK_α radiation). The film structure and the phase composition were studied with transmission and diffraction electron microscopy using a PREM-200 transmission electron microscope. The measurements of saturation magnetization were carried out with a torsion magnetometer. The magnitudes of the polar effect K_{eff} (θ_k) and the Faraday (θ_F) effects as well as their spectral dependencies were measured in magnetic fields up to 14 kOe with the technique of zero-analyzer

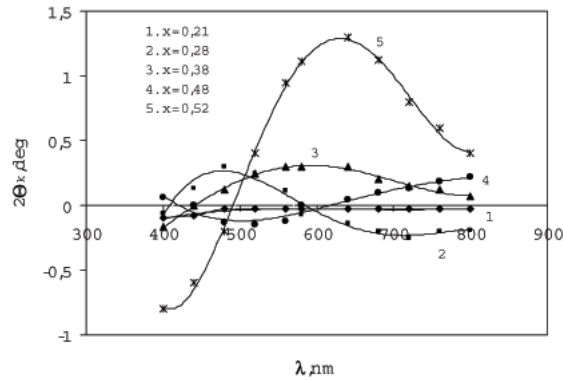


Fig. 2. Spectral dependences of the Kerr rotation angle of the nanogranular Co-Ti-O films with the filling factor of the magnetic phase $X = (1) 0.21, (2) 0.28, (3) 0.38, (4) 0.48,$ and $(5) 0.52$

with double modulation of the polarization plane of the incident light. Measurements were made at room temperature in the wavelength range of 350-1000 nm. The accuracy of measurement was equal to ± 0.2 min. The coercive force (H_c) was defined from the magneto-optical hysteresis loops.

For the phase identification of products of the solid-state reactions in layered CoO/Ti structure, we performed X-ray diffraction studies of the structure before and after reaction performed under aforementioned conditions

In Fig. 1a X-ray diffraction pattern of the layered CoO/Ti structure with the relative volume of the magnetic phase $X = 0.4$ is presented. This picture contains the reflection from the CoO phase. There are no titanium reflection in the X-ray diffraction pattern, which is likely indicative of the formation of amorphous titanium. Note that research of the structure of the titanium films of 300 nm thickness, obtained at the same conditions, also shows the formation of an amorphous structure.

Fig.1b shows the X-ray diffraction pattern of the layered structure described above after carrying out the solid-state reaction at a temperature 670 K and a pressure 1×10^{-6} Torr in the vacuum chamber. The diffraction picture contains a peak which can be attributed to both cubic and hexagonal Co. Apparently, diffraction peaks of the titanium compounds are absent in the diffraction pattern, which is indicative of amorphous structure of titanium oxides. The latter does not contradict the data in [12] specifying the formation of the amorphous titanium oxide films with a thickness of up to 35 nanometers at a substrate temperature no higher than 620 K. In the work [13] the authors observe a sedimentation of amorphous oxide of titanium at temperature of the substrate not more than 720 K.

The electron microscopy investigations of the film with $X = 0.56$ after carrying out the solid-state reaction, obtained on a single-crystal NaCl substrate, have shown, that the film consists of fine crystallites with the size of 10-20 nm and bigger crystallites with the size of 50-100 nm.

As a result of the interpretation of the electron diffraction pattern, we established that the film after carrying out the reaction contains the following phases: Co (hcp), CoO, Co_2TiO_4 .

In the electron diffraction pattern, the reflections corresponding to the CoO and Co_2TiO_4 phases have the shape of rings characteristic of polycrystals, and point reflections corresponding to the hcp Co phase. On the basis of this fact, we can conclude that the CoO and Co_2TiO_4

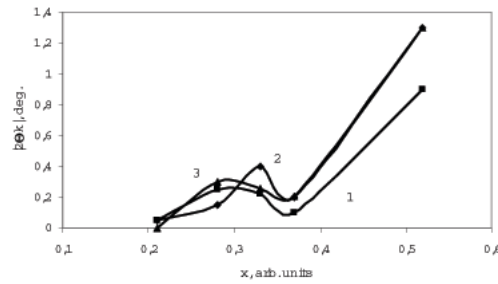


Fig. 3. Dependence of the Kerr rotation angle on the filling factor of the magnetic phase (1) in the case of the maximum angle, (2) at the wavelength 700 nm, and (3) at the wavelength 630 nm

phases are in fine-grained state (the crystallite size is 10-20 nm), and form an original matrix in which bigger Co crystallites (the size is 50–100 nm) are located.

Apparently, in this case the dielectric matrix has complex phase composition. The presence of the CoO phase can be explained, to some extent, by the fact that, on the one hand, the reaction with oxygen exchange in the layers does not occur through all depth, and on the other hand, there is an excess CoO at $X = 0.56$ with respect to the equilibrium content ($X = 0.4$). The formation of the Co_2TiO_4 compound in the dielectric matrix is unexpected likely due to the variety of phases in Co-Ti-O system. Likely, the conditions of solid-state reaction should be optimized.

Thus, the X-ray diffraction and electron microscopy investigations of the films synthesized under conditions of the isothermal reaction in the layered CoO/Ti structures unambiguously show that metallic Co is formed among the products of the reaction (1). The presence of the dielectric matrix is confirmed by the high values of the electrical resistivity of the sample in the investigated magnetic-phase concentration range ($10^{-3} - 10^{-1} \Omega \text{ m}$).

The research of magnetic properties of the obtained nanogranular Co-Ti-O films shows the following.

The magnetization reversal curves of the Co-Ti-O films measured by the magneto-optical method (polar Kerr effect) in a magnetic fields up to 14 kOe, for the composition with the volume concentration of the magnetic phase $X = (0.3 - 0.52)$ exhibit a ferromagnetic character, and curves for concentration of 0.21 does not have any hysteresis, what is indicative of the superparamagnetic state [11,14].

The magneto-optical spectra of the obtained films were investigated in the visible optical range in a magnetic field up to 14 kOe. Fig. 2 shows the spectral dependences of Kerr rotation for the nanogranular films with various filling factor (volume concentration) of the magnetic phase (Co). Apparently the spectral curves are nonmonotonic. For the structure with $X = 0.52$ the curve shows resonance character with substantial increase in Kerr rotations angle in the wavelength range of 500–700 nm.

Fig. 3 shows the dependence of the absolute value of maximum Kerr rotation angle and also the values of the angle at wavelength of 630 and 700 nm on the filling factor of the magnetic phase X . It is necessary to note, that the observed features in the Kerr effect spectrum of the obtained nanogranular films are characteristic of inhomogeneous metal-isolator media [3–7].

The dependencies (Fig. 3) have two regions of an increase in the rotation angle, one of which is in the subpercolation region and the other region is near the percolation threshold. The

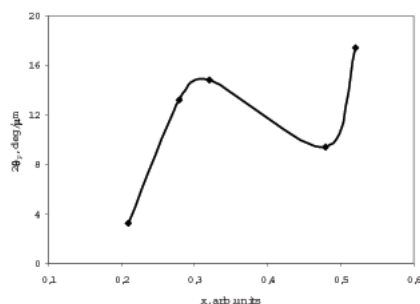


Fig. 4. Dependence of the specific Faraday rotation on the filling factor of the magnetic phase X at the wave-length of 630 nm

first maximum was observed in work [5] and was connected, in opinion of the authors, with the interference effects. The second region is likely explained by the percolation [5, 6].

The study of the Faraday rotation spectra of the obtained films has shown the following. The starting layered CoO/Ti structure, which was not subjected to annealing, is characterized by the presence of the Faraday rotation. This testifies the fact that the solid-state reaction occurs even during deposition of the titanium layer on the cobalt oxide layer in spite of the arbitrarily cold substrate (320 K). So, before annealing, the specific Faraday rotation of the films with the filling factor of the magnetic phase $X = 0.46$ at a wavelength of 630 nm is 6.5 degree/ μm . Annealing leads to the increase of the Faraday rotation to 12 degree/ μm . The Faraday rotation spectra, as well as the Kerr rotation spectra, are nonmonotonic. Fig. 4 shows the dependence of the specific Faraday rotation angle on the X at wavelength of 630 nm. It should be noted that there is a correlation between the filling factor dependences of the Kerr and Faraday rotations (compare with curve 3 in Fig. 3).

Let us note the basic results of the investigations of physical properties of the nanogranular Co-Ti-O films obtained under conditions of the solid-state reactions in layered CoO/Ti structures.

The products of the solid-state reaction in layered structure CoO/Ti in the isothermal annealing mode are metallic Co and amorphous Ti-O compounds. The nanogranular films are metallic cobalt particles embedded in a dielectric matrix. The shape of the magnetization reversal curves for the samples with $X = (0.3 - 0.52)$ testifies to the ferromagnetic interaction between magnetic regions.

The magneto-optical spectra of the Kerr effect of the films with filling factor of magnetic phase from 0.3 to 0.52 are nonmonotonic, unlike the spectrum of the uniform Co film. In the wavelength range of 550–700 nm, the Kerr rotation angle of the films with $X = 0.52$ increases by a factor of 2–2.5 compared to conventional Co films. The correlation between the filling factor dependences of the Kerr and Faraday rotations is established.

The work was supported by the Russian Foundation for Basic Research (RFBR projects no. 08-02-00397-a, no. 07-03-00190-a).

References

- [1] L.V. Lutsev, Yu.E. Kalinin, A.V. Sitnikov et. al., Electron transport in magnetic field of granular amorphous silica dioxide films with ferromagnetic nanoparticles, *Fiz. Tverd. Tela*,

- 44(2002), no. 10, 1802 (in Russian).
- [2] J.C. Denardin, M. Knobel et. al., Giant Hall effect in superparamagnetic granular films, *J. Magn. Magn. Mater.*, **262**(2003), no. 1, 12.
- [3] V.G. Kravets, L.V. Poperenko, I.V. Yurglevych et. al., Optical and magneto-optical properties and magnetorefractive effect in metal-isolator CoFe-Al₂O₃ granular films, *J. Appl. Phys.*, **98**(2005), no. 4, 043705.
- [4] V.S. Zhigalov, R.D. Ivantsov, I.S. Edelman et. al., Faraday effect in Co-Sm-O nanogranular films, *Fiz. Tverd. Tela*, **47** (2005), no. 6, 91 (in Russian).
- [5] A.M. Kalashnikov, V.V. Paul, R.V. Pisarev et. al., Optical and magneto-optical properties of CoFeB/SiO₂ and CoFeZr/Al₂O₃ nanogranular structures, *Fiz. Tverd. Tela*, **46**(2004), no. 11, 2092 (in Russian).
- [6] Z.S. Jiang, G.J. Jin, J.T. Ji et. al., Magneto-optical Kerr effect in Fe-SiO₂ films, *J. Appl. Phys.*, **78**(1995), no. 1, 439.
- [7] A.V. Kimel, R.V. Pisarev, A.A. Rzhevsky, Magneto-optical investigation of granular films of oxide silica with CoNbTa particles, *Fiz. Tverd. Tela*, **45** (2003), no. 2, 269 (in Russian).
- [8] G.I. Frolov, Film medium for memory devices with superdense magnetic record, *JTP*, **71**(2001), no. 8, 50.
- [9] M. Abe, M. Gomi, Magneto-optical effect and effective dielectric tensor in composite material containing magnetic fine particles or thin layers, *Jpn. J. Appl. Phys.*, **23**(1984), no. 12, 1580.
- [10] Yu.A. Dynnik, I.S. Edelman, T.P. Mopozova et. al., Faraday effect in Co/TiO₂ films, *JETP Lett.*, **65**(1997), no. 7-8, 531.
- [11] V.G. Miagkov, K.P. Polyakova, G.N. Bondarenko, V.V. Polyakov, Granular Fe-Al₂O₃ films prepared by self-propagating high temperature synthesis, *J. Magn. Magn. Mater.*, **258-259**(2003), no. 2, 358.
- [12] L. Holland, Vacuum Deposition of Thin Films (New Work, 1956; Gosenergoizdat, Moscow, 1962).
- [13] M. Lottiaux, C. Boulesteix et. al., Morphology and structure of TiO₂ thin layers vs. thickness and substrate temperature, *Thin Solid Films*, **170**(1989), no. 1, 107.
- [14] D. Kumar, J. Narayan, A.V. Rvity et. al., High coercivity and superparamagnetic behavior of nanocrystalline iron particles in alumina matrix, *J. Magn. Magn. Mater.*, **232**(2001), no. 1, 161.

Магнитооптические свойства наногранулированных пленок Co-Ti-O

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В работе представлены результаты исследования структурных и магнитооптических свойств наногранулированных пленок Co-Ti-O, полученных в условиях твердотельной реакции с обменом кислородом в слоистых структурах CoO/Ti. Показано образование гранулированных пленок составов в области и ниже порога перколяции. Обнаружены особенности магнитооптических спектров пленок с коэффициентом заполнения магнитной фазы от 0.3 до 0.51 в сравнении со спектрами сплошных пленок металлов.

Ключевые слова: наногранулированные пленки, твердотельные реакции, синтез, магнитооптические свойства, эффект Керра.