
MAGNETISM
AND FERROELECTRICITY

Synthesis and Magneto-Optical Properties of Nanogranular Co–Ti–O Films

V. V. Polyakov^a, K. P. Polyakova^{a,*}, V. A. Serezhkin^a, and S. M. Zharkov^{a,b}

^a *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

^{*} *e-mail: pkp@iph.krasn.ru*

^b *Siberian Federal University, pr. Svobody 79, Krasnoyarsk, 660041 Russia*

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Abstract—Studies of the structural and magneto-optical properties of nanogranular Co–Ti–O films prepared under conditions of the solid-state reaction with oxygen exchange in the CoO/Ti layered structures are presented. The formation of granular films with compositions near or below the percolation threshold is shown. The specific features of the magneto-optical spectra of the prepared films as compared to the spectra of continuous metallic films are revealed.

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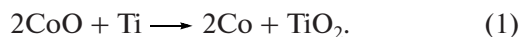
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Nanogranular films consisting of ferromagnetic grains embedded in a dielectric matrix have attracted enhanced interest of researchers owing to their unusual properties. It should be noted first the anomalous Hall effect, tunneling magnetoresistance, magnetorefractive effect, and enhancement of the magneto-optical effects.

Most of studies are dealing with granular films in SiO₂ and Al₂O₃ dielectric matrices. Theoretical calculations have shown that the magneto-optical spectra in inhomogeneous systems, unlike the spectra of continuous films, depend on the filling factor of the magnetic fraction (or the relative volume of the magnetic fraction) and the type of the dielectric matrix [1]. In this connection, of interest are the magneto-optical properties of the granular films in the TiO₂ matrix with the dielectric constant exceeding the dielectric constants of SiO₂ and Al₂O₃.

We have shown previously that the products of the solid-state reactions occurring in the layered Fe₂O₃/Al and Fe₂O₃/Ti structures with oxygen exchange in the layers are Fe nanoparticles embedded in the Al₂O₃ and TiO₂ dielectric matrices, respectively [2, 3]. In this case, the oxide matrixes have a noncrystalline or amorphous structure.

Taking into account the high chemical activity of titanium with respect to oxygen, in order to prepare granular Co films in a dielectric matrix of titanium oxide, we used the reaction



Here, CoO and Ti layers on a substrate can serve as reagents. It follows from Eq. (1) that the relative volume of the magnetic phase in the reaction products is 0.4. In order to change the ratio of volumes of the

magnetic and dielectric phases in the reaction products, it is necessary to change not only the ratio of the reagent layer thicknesses but also the pressure of residual gases. It is simpler to prepare films with the concentration of the magnetic phase in the reaction products near 0.4 and lower. In this case, cobalt is reduced completely and the titanium excess with respect to the equilibrium content in reaction (1) can be oxidized during annealing.

In this work, the results of the synthesis of the composite films with the relative volumes $X = 0.2–0.52$ during isothermal annealing at a temperature of 620–670 K and a pressure of $10^{-6}–10^{-5}$ Torr are presented.

The CoO films were prepared by oxidation (at a temperature of 670 K in air) of the cobalt films deposited on cover-glass plates by thermal evaporation under vacuum at a residual pressure of $\sim 10^{-6}$ Torr and a temperature of 470–520 K. The titanium layers were deposited by ion-plasma sputtering of a bulk titanium target at a pressure of $(4–5) \times 10^{-4}$ Torr and a substrate temperature of ~ 320 K. The solid-state reaction was performed during isothermal annealing at a temperature of 620–670 K under vacuum at a residual pressure of $10^{-6}–10^{-5}$ Torr. The temperature of the solid-state reaction was chosen to be identical to that for the solid-state reaction $\text{Fe}_2\text{O}_3 + 1/2\text{Ti} \longrightarrow 2\text{Fe} + 1.5\text{TiO}_2$ [2]. We prepared the structures with volume fractions of the magnetic phase $X = 0.2–0.52$. Here, $X = V(\text{Co})/V(\text{Co} + \text{Ti–O})$.

The chemical composition and thickness of the prepared samples were determined using the X-ray fluorescence analysis. The X-ray diffraction patterns were recorded on a DRON-3 diffractometer (CuK_α radiation). The saturation magnetization was mea-

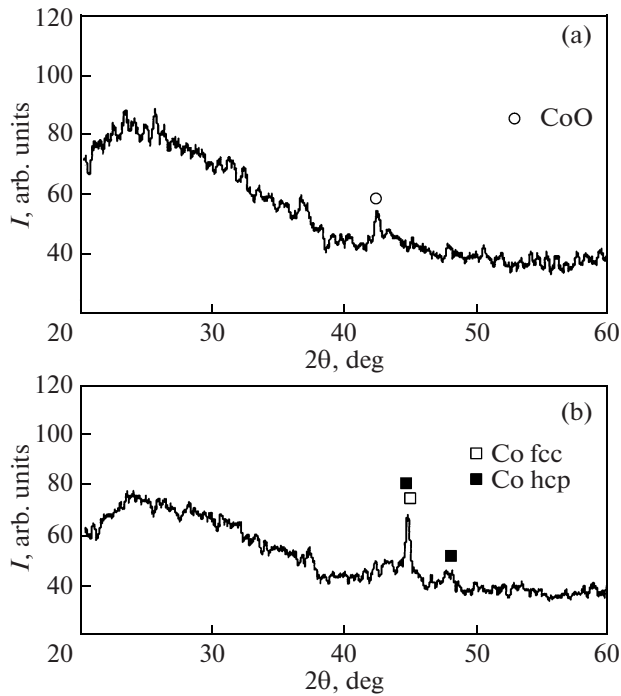


Fig. 1. X-ray diffraction patterns of the layered CoO/Ti structure (a) before and (b) after annealing.

sured on a torsion magnetometer. The film structure and phase composition were studied by transmission and diffraction electron microscopy using a PREM-200 transmission electron microscope. The magnitudes of the polar magneto-optical Kerr effect θ_k and Faraday effect θ_F , as well as their spectral dependences, were measured on a magneto-optical device in fields up to 14 kOe using a technique of null-analyzer with double azimuth modulation of the polarization plane of incident light. The measurements were performed at room temperature in the wavelength range 350–1000 nm. The measurement accuracy was 0.2'. The coercive force H_c was found from the magneto-optical hysteresis loops.

To identify the phases of the products of the solid-phase reaction in the layered CoO/Ti structure, we performed X-ray diffraction studies of two-layer CoO/Ti structure on a cover-glass substrate before the reaction and after reaction performed under aforementioned conditions.

Figure 1a shows the X-ray diffraction pattern of the layered CoO/Ti structure with the relative volume of the magnetic phase $X = 0.4$. This pattern contains the reflection from the CoO phase. There are no titanium reflections in the X-ray diffraction pattern, which is likely indicative of the formation of amorphous titanium. Note that the study of the structure of titanium films ~ 300 nm in thickness prepared under identical conditions also shows the formation of an amorphous structure.

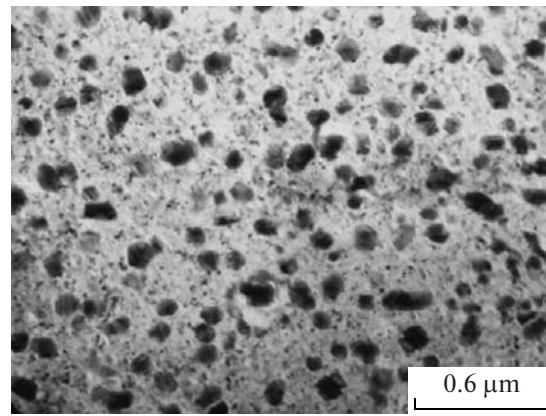


Fig. 2. Electron microscope image of the CoO/Ti film after the reaction.

Figure 1b shows the X-ray diffraction pattern of the layered structure described above after performing the solid-state reaction at a temperature of 670 K and a pressure of 1×10^{-6} Torr in the vacuum chamber. The diffraction pattern contains a peak that can be attributed to both cubic and hexagonal Co. There are no diffraction peaks of the titanium compounds in the diffraction pattern, which is indicative of amorphous structure of titanium oxides. The latter does not contradict the data from [4], which are indicative of the formation of amorphous titanium oxide films with a thickness of up to 35 nm at a substrate temperature of no higher than 620 K. In [5], deposition of amorphous titanium oxides was noted at a substrate temperature of no higher than 720 K.

The electron microscopy studies of the films with $X = 0.56$ prepared on a single-crystal NaCl substrate after performing the solid-state reaction show that the films consist of fine crystallites with sizes of ≈ 10 – 20 nm and coarser crystallites with sizes of ≈ 50 – 100 nm (Fig. 2).

As a result of the interpretation of the electron diffraction pattern, we established that the film after performing the reaction contains the following phases:

- (i) Co with a hexagonal close-packed (hcp) lattice, space group $P6_3/mmc$, and the lattice parameters $a = 2.503 \text{ \AA}$ and $c = 4.0605 \text{ \AA}$ (JCPDS card no. 05-0727);
- (ii) CoO with a cubic structure, space group $Fm\bar{3}m$, and the lattice parameter $a = 4.260 \text{ \AA}$ (JCPDS card no. 09-0402);
- (iii) Co_2TiO_4 with a cubic structure, space group $Fm\bar{3}m$, and the lattice parameter $a = 8.4348(2) \text{ \AA}$ (JCPDS card no. 39-1410).

In the electron diffraction pattern, the reflections belonging to the CoO and Co_2TiO_4 phases have the shape of rings characteristic of polycrystals and the point reflections belong to the hcp Co phase. Based on this fact, we can conclude that the CoO and Co_2TiO_4 phases are in a fine-grained state (crystallite size ≈ 10 –

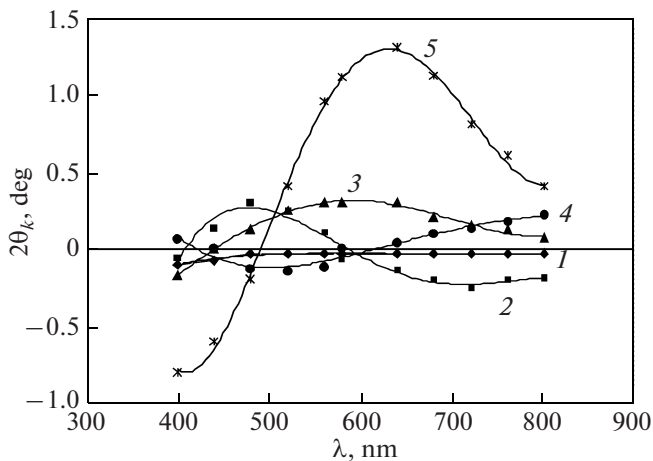


Fig. 3. Spectral dependences of the Kerr rotation angle of the nanogranular Co–Ti–O films with volume fractions of the magnetic phase $X = (1)$ 0.21, (2) 0.28, (3) 0.38, (4) 0.48, and (5) 0.52.

20 nm) and form a peculiar kind of matrix in which coarser Co crystallite (size ≈ 50 –1000 nm) are located.

As is seen in this case, the dielectric matrix has a 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 and is likely due to a variety of phases in the Co–Ti–O system. Likely, the conditions of the solid-state reaction should be optimized.

Thus, the X-ray diffraction and electron microscopy studies 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 reaction (1). The presence of the dielectric matrix is confirmed by the high electrical resistivity of the samples over the magnetic-phase concentration range under study (10^{-3} – $10^{-1} \Omega \text{ m}$).

The study of the magnetic properties of the nanogranular Co–Ti–O films prepared shows the following.

The magnetization reversal curves for the Co–Ti–O films measured by the magneto-optical method (the polar Kerr effect) in 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 those for a concentration of 0.21 have no any hysteresis, which is indicative of the superparamagnetic state [2, 6].

The magneto-optical spectra of the films prepared were studied in the visible optical range in magnetic fields up to 14 kOe. Figure 3 shows the spectral dependences of the Kerr rotation for the nanogranular films

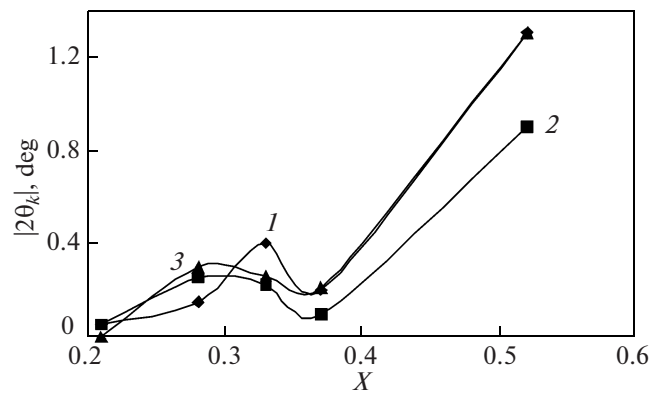


Fig. 4. Dependences of the Kerr rotation angle on the volume concentration of the magnetic phase (1) in the case of the maximum angle, (2) at a wavelength of 700 nm, and (3) at a wavelength of 630 nm.

with different concentrations of the magnetic phase (Co). It is seen that the spectral curves are nonmonotonic. For the structure with $X = 0.52$, the curve exhibits a resonance character with a significant increase in the Kerr rotation angle in the wavelength range 500–700 nm.

Figure 4 displays the dependences of the magnitude of the maximum Kerr rotation angle and the magnitudes of the angle at wavelengths of 630 and 700 nm on the relative volume of the magnetic phase X . It should be noted that the observed peculiarities in the Kerr-effect spectrum of the nanogranular films prepared are characteristic of inhomogeneous metal–insulator media [7–9].

The concentration dependences (Fig. 4) 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 first maximum was observed by Kalashnikova et al. [9], who assumed that it is associated with the interference effects. The second region is likely explained by the percolation [9, 10].

The study of the Faraday-rotation spectra of the films prepared shows the following. The starting layered CoO/Ti structure, which was not subjected to annealing, is characterized by the presence of the Faraday rotation. This indicates 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 volume fraction of the magnetic phase $X = 0.46$ at a wavelength of 630 nm is $6.5 \text{ deg}/\mu\text{m}$. Annealing increases the Faraday rotation to $12 \text{ deg}/\mu\text{m}$. The Faraday rotation spectra, as well as the Kerr rotation spectra, are nonmonotonic. Figure 5 shows the dependence of the specific Faraday rotation angle on the magnetic-phase concentration at a wavelength of 630 nm. It should be noted that there is a correlation between the concen-

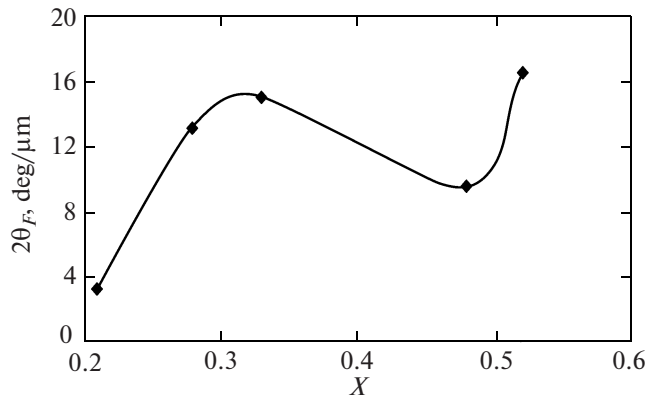


Fig. 5. Dependence of the specific Faraday rotation on the volume concentration of the magnetic phase X at a wavelength of 630 nm.

tration dependences of the Kerr and Faraday rotations (compare with curve 3 in Fig. 4).

Let us note the main results of the performed studies of the physical properties of the nanogranular Co–Ti–O films prepared under conditions of the solid-state reactions in the layered CoO/Ti structures.

The products of the solid-state reaction in the layered CoO/Ti structure in the regime of isothermal annealing are metallic Co and amorphous Ti–O compounds. The nanogranular films are metallic Co particle embedded in a dielectric matrix. The shape of the magnetization reversal curves for the samples is indicative of the ferromagnetic interaction between magnetic regions.

The magneto-optical spectra of the Kerr effect of the films with the relative volume of the magnetic fraction from 0.3 to 0.52 are nonmonotonic, unlike the spectrum of the continuous Co film. In the wavelength range 550–700 nm, the Kerr rotation angle increases by a factor of 2–2.5 compared to conventional Co films. The correlation between the concentration

dependences of the Kerr and Faraday rotations is established.

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