Magnetotransport properties of $Co_x(MgF_2)_{100-x}$ oxygen-free nanocomposites

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Abstract. Electric and magnetoresistive properties of $Co_x(MgF_2)_{100-x}$ thin films ($14 \leq x$, ат. $\% \leq 62$) were investigated. It is established that the received films have a composite structure. Magnetoresistive and electric properties of the films in initial state and after heat treatment have been investigated. The magnetoresistive effect of the studied samples in initial state reaches 7,5% in magnetic field of 10 kOe. It is established that the composites structure is steady against thermal heating up to 250 °C. The change of composites magnetoresistive effect after heat treatment depends on the Co concentration. The particularities of the magnetoresistive changes after annealing are discussed.

Introduction

One of the most characteristic properties of nanogranular ferromagnetic metal-insulator composites is the tunneling magnetoresistance (TMR). High values of TMR have been observed in cobalt based composites [1]: in Co-Al-O composites the magnetoresistance reaches 7-8 % [2] and in some cases it reaches 10 % [3]. Despite the high values of the TMR observed in the composites the presence of an oxide matrix leads to some undesirable phenomena. In particular the metal phase can be oxidized during deposition and subsequent storage of the composites. The oxidizing affects to the properties of the formed samples usually worsening them. The aim of the present work was to obtain a two-phase metal-insulator nanocomposite based on an oxygen-free matrix capable to exhibit high values of the magnetoresistive effect and save these values under thermal action.

Experimental procedure

The Co-MgF_2 system was chosen as an object of investigation. Magnesium fluoride was selected as the dielectric phase since the formation of MgF_2 is much more energetically favorable than the formation of CoF_2. That ensures the production of a composite structure in the chosen system. All samples have been prepared by ion-beam sputter of mosaic target made from a Co base and MgF_2 plates nonsymmetrically located on its surface. The samples were deposited out on glass (for structure investigations) and glassceramic substrates (for resistive measurements).

The elemental composition of the composites was determined by electron-probe energy-dispersive microanalysis. The measurements were carried out on a scanning X-ray microanalyzer JXA-840 with an error not exceeding 1.5% of the content of the measured element. The thickness of the obtained samples was monitored with the help of the MII-4 interferometer. A BRUKER D2 Phaser diffractometer was used to perform the phase analysis of the samples.

Investigation of the magnetoresistive effect was carried out by direct measurement of the electrical resistivity of the samples during the change of the external magnetic field. The resistance of the samples was measured by a potentiometric method using a two-probe DC method. The error of the electrical resistivity measurements did not exceed 0.1%. Annealing of the samples was carried out in a vacuum with a residual pressure not less than 10^{-3} Torr.

Results

As a result of the deposition the samples of $Co_x(MgF_2)_{100-x}$ fine-dispersed thin-films were obtained. The thickness of the investigated films is 1-3 μm depending on the composition. The concentration of the metal phase in the obtained samples smoothly changes from 14 to 62 atomic %.

Analysis of the diffractograms obtained from the samples in the initial state indicates the presence of a two-phase (composite) structure for all obtained compositions (fig. 1). There are peaks corresponding only to two phases: magnesium fluoride and cobalt on the diffractograms. As can be seen from Figure 1 the peaks corresponding only to the MgF_2 phase are observed on the diffractograms corresponding to the lower metal concentration. As the concentration of the metal increases the intensity of the peaks of the dielectric component decreases and the peaks from the crystalline Co with hexagonal structure become more pronounced.

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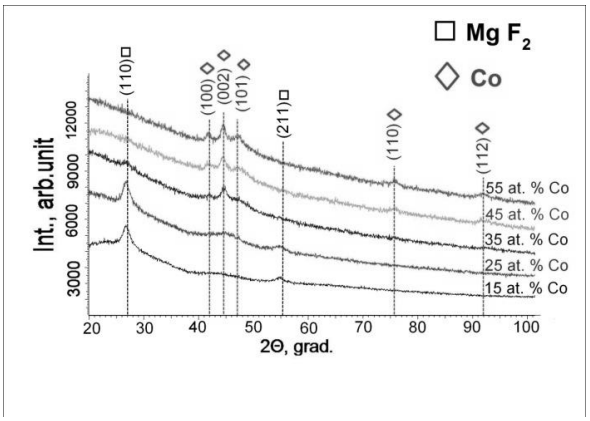

Fig. 1. Diffractograms of $Co_x(MgF_2)_{100-x}$ samples. The cobalt concentration (in at. %) is indicated by the numbers

It is wellknown that the electrical properties of any nanogranular composite system change radically with increasing of metal phase concentration [4]. In particular, the concentration dependence of the resistivity of $Co_x(MgF_2)_{100-x}$ composites in the initial state is typical for composite metal-insulator systems (fig. 2).

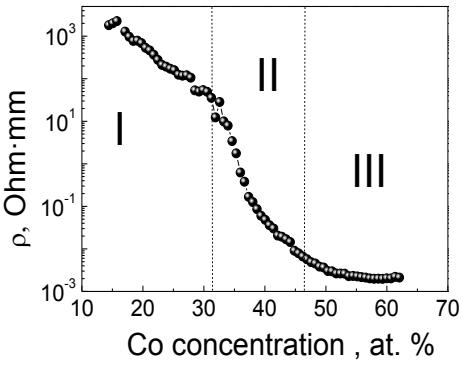

Fig. 2. Concentration dependence of the electrical resistivity of $Co_x(MgF_2)_{100-x}$ composites. The data are obtained at room temperature

The whole studied concentration range can be divided into three regions, differing from each other by the angle of inclination of the ρ dependence. The second region is characterized by a sharp decrease of resistance against the background of a relatively small change in Co concentration. Thus, it can be concluded that this region of concentration dependence corresponds to the percolation threshold [5]. An estimation of the concentration position of the percolation threshold for the $Co_x(MgF)_{100-x}$ system corresponds to an interval of 30-36 at.% Co (fig. 2).

In the vicinity of the threshold the $Co_x(MgF)_{100-x}$ samples exhibit magnetoresistive effect. It reaches quite high values even at relatively small applied field (fig. 3). In a case of larger magnetic field (up to 10 kOe) maximum values of the tunnel magnetoresistance reaching 7.5% (fig.3, incert). However, it should be noted that even in the region of the TMR maximum the saturation of the effect is not achieved (fig. 3, inset) and can be larger in a case of the field increasing. One should note that the presence of the magnetoresistive effect unambiguously confirms the compositeness of the samples.

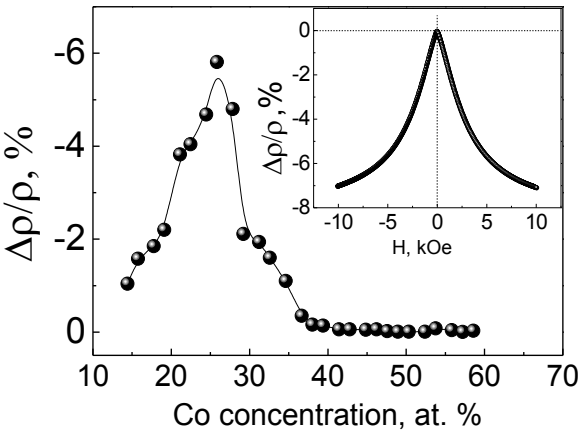

Fig. 3. The concentration dependence of the magnetoresistive effect of $Co_x(MgF_2)_{100-x}$ composites in the initial state. The TMR values were determined in a field of 5 kOe. The inset shows the field dependence of TMR for $Co_{25}(MgF_2)_{75}$. The data are obtained at room temperature

Nanogranular composites prepared by deposition technique has a nonequlibrium structure and any thermal influence should change physical properties of the material. To determine the thermal stability of the prepared composites the electrical resistance versus temperature has been measured in some samples (fig. 4). As follows from the presented data the heating of the samples to a temperature of 250 °C affects their electrical resistance in different ways. The resistance of the samples with a concentration corresponding to the pre-threshold interval increases with temperature increasing and after cooling it is higher than in the initial state (for example $Co_{24}(MgF)_{76}$, fig. 4). In samples with a higher cobalt concentration (31 at.% Co and above) the resistance begins to decrease during heating and after cooling it is lower than in the initial state (fig. 4).

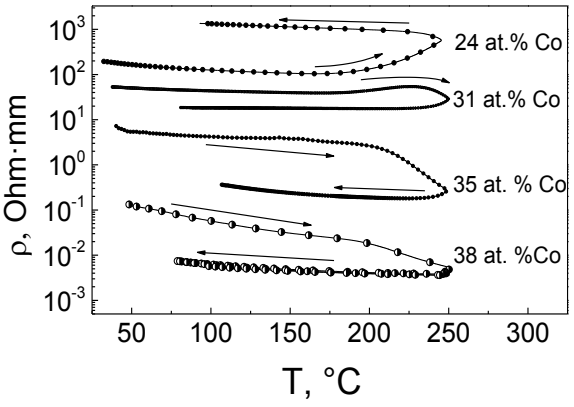

Fig. 4. Temperature dependence of the electrical resistivity of $Co_x(MgF_2)_{100-x}$ composites

The analysis of the obtained data also indicates that no structural changes occur in composites up to 200 °C. This follows from the fact that the resistance of the samples varies practically linearly in this temperature interval without any anomalies.

A more significant argument in favor of the fact that the structure of composites does not undergo any changes in this temperature interval is the absence of any change in the

TMR values (fig. 5). If the samples annealing was carried out at 180 °C it did not lead to any changes in the TMR values (fig. 5). This fact testifies the stability of both the samples dielectric matrix and the composite structure as a whole. The invariance of the TMR values may also indicate a low level of defectiveness of the fluoride matrix. In the opposite case the defect concentration should decrease during annealing and as a consequence the TMR values should increase [6] but such result is not observed in our experiment.

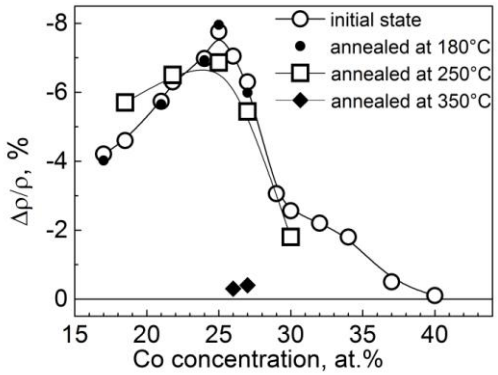

Fig. 5. The concentration dependence of the magnetoresistance of $Co_x(MgF_2)_{100-x}$ composites in the initial state and after heat treatment. All TMR values (for as-deposited and annealed samples) were determined in a field of 10 kOe at room temperature

Heating the samples to 200 - 250 °C initiates the beginning of structural changes which result in a significant change of the resistance (at room temperature the difference of the samples resistance in the initial state and after heat treatment at 250 °C is almost one order or larger, see Figure 4). Moreover, this annealing procedure changes the TMR values. The change of the TMR is systematic: the TMR value increases in the composites with low Co concentration (before the percolation threshold) but the TMR decreases in the composites located beyond the threshold (fig. 5).

A similar reaction of composites on the thermal action was observed in oxide-based composites (CoFeB-SiO_2) [7]. The magnetoresistance of the composites decreased after annealing if the concentration of metal phase was larger than the percolation threshold. On the contrary the TMR values increased after heat treatment if the metal concentration was lower than the percolation.

An increase of the heating temperature up to 350 °C leads to a significant change of the $Co_x(MgF_2)_{100-x}$ composites resistance. The resistance of the composites lying before the percolation threshold increases by several orders of magnitude and reaches hundreds of MΩ which does not allow to fulfill the potentiometric measurements (fig. 6). The resistance decreases sharply and the sign of the temperature coefficient of electrical resistance (α) changes from negative to positive if the composites located behind the percolation threshold. The positive α sign is typical for the metallic conductivity mechanism and indicates the formation of the percolation cluster after treatment at 350 °C. Such significant changes of electrical resistance indicate either interfacial interaction or significant changes in the properties of the phases themselves, provided that the heterogeneity (compositness) of the samples is preserved.

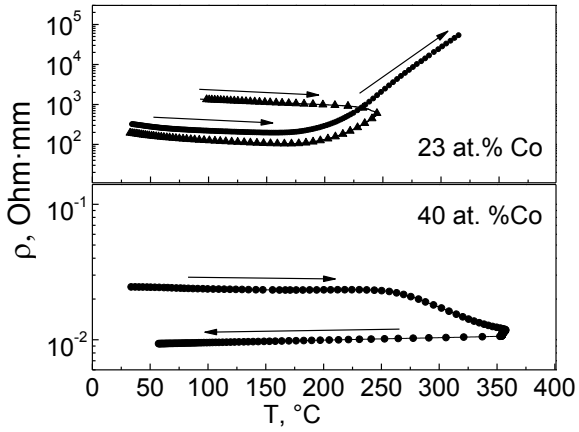

Fig. 6. Temperature dependence of electrical resistance for two $Co_x(MgF_2)_{100-x}$ composites located before and after percolation threshold

To detect the possible changes in the structure of the composites the X-ray structural studies of samples annealed at 350 ° C for 10 min were performed Figure 7 shows the diffraction patterns of the samples in the initial state and after heating at 350 °C. Obviously, the temperature influence does not affect the shape of the diffractograms: only an increase in the intensity of the peaks and a change in their shape are observed. The diffraction peaks became higher and narrower which indicates an increase in the size of the coherent scattering.

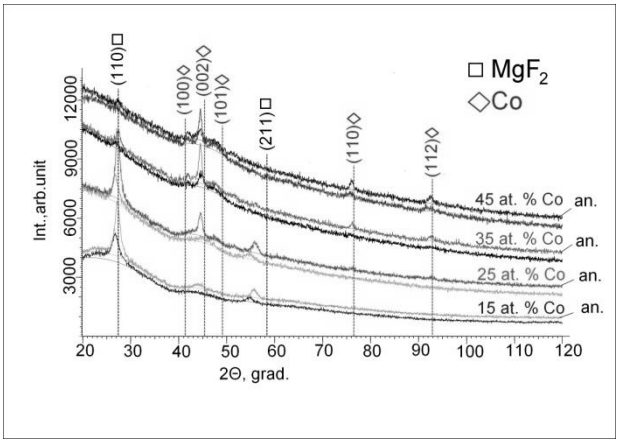

Fig. 7. Diffractograms of $Co_x(MgF_2)_{100-x}$ samples in the initial state (bottom curve for each sample) and after annealing at T = 350 °C (upper curve, indicated by symbol "an."). The Co concentration (in at. %) is indicated by the numbers

Using the Sherrer method, which takes into account the half-width of the diffraction maximum, the source wavelength, and also the Bragg diffraction angle, the values of the coherent scattering regions (L) were calculated for the cobalt phase. It seems quite reasonable to assume that the regions of coherent scattering in the metallic phase are the cobalt nanogranules. The results of calculations are presented in Table 1.

The growth of cobalt granules is obvious and for the composite located on the percolation threshold the increase reaches more than 100%. Such increase of the metal

granules size explains the sharp decrease of the TMR to practically zero in composites located beyond the percolation threshold after heat treatment at 350 °C (fig. 5).

Table 1. The size of the cobalt grains in the initial state and after annealing at T = 350 °C.

	L, nм	
Composition	Initial state	After annealing at T = 350 °C
$Co_{25}(MgF_2)_{75}$	4,5	10,6
$Co_{35}(MgF_2)_{65}$	8,5	13,3
$Co_{45}(MgF_2)_{55}$	11,3	15,6

First, as the size of the metal granules increases, the width of the dielectric barrier should decreases. Thus, interaction can take place between the granules that leads to the formation of large magnetic domains (magnetic clusters). The magnetic moments of individual granules do not depend on the external magnetic field within this domain size. This local region of the composite does not contribute to the formation of the magnetoresistive effect (the conductivity through such a domain does not depend on the magnetic field). The second reason for the reduction of the TMR after annealing is the formation of electric percolation clusters, where electrical conductivity is due to the usual metallic conductivity while the tunneling does not occur. The formation of percolation clusters and the change of the conductivity mechanism are confirmed by the temperature dependences of the electrical resistivity of the composites with large cobalt content (behind the percolation threshold. fig. 6).

In pre-percolation composites the situation is different. Their morphology (and, consequently, their nanogranular structure) remains practically unchanged (fig. 7). However, in this case, the resistance increased to such high values that it did not allow to correctly determine the magnitude of the TMR effect. A possible explanation for this fact is a significant reduction in the degree of defectiveness of the dielectric matrix as a result of annealing at 350 C. It is known that in composites in addition to direct tunneling of electrons between the granules the hopping conductivity along the defects of the dielectric matrix also exists [6]. In our case, such defects are the broken bonds of magnesium atoms and cobalt atoms dissolved in fluoride. During the annealing the cobalt atoms diffuse to the granules increasing their size and the broken magnesium bonds can be connected by oxygen contained in the residual gas of the vacuum chamber.

As a result of these processes, the electrical resistivity of composites should increase, which is observed in our experiments (fig. 6). Also, the result of these processes should be the growth of the magnetoresistive effect. It should be noted that heating of the pre-percolation composites to a lower temperature (fig. 4, fig 5) leads precisely to this result: the growth of resistance and the growth of the magnetoresistive effect.

Conclusion

The nanocrystalline composites $Co_x (MgF_2)_{100-x}$ ($14 \leq x$, at.% $Co \leq 62$) were prepared by ion-beam sputtering of a composite target in an argon atmosphere. Composites exhibit a tunneling magnetoresistance, reaching 7.5% in fields of 10 kOe. Composites exhibit thermal stability with respect to heating to 250 °C, while maintaining high TMR values.

Acknowledgment

The work has been partly supported by RFBR grant № 15-02-05920_a

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