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Ferromagnetic resonance spectroscopy of CoFeZr-Al_2O_3 granular films containing “FeCo core – oxide shell” nanoparticles

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ABSTRACT

Ferromagnetic resonance (FMR) spectroscopy is applied for comparative analysis of granular $(CoFeZ)_x(Al_2O_3)_{100-x}$, (31 at% ≤ x ≤ 47 at%) films containing pure FeCo-based nanoparticles (NPs) or “FeCo-based core – oxide shell” NPs inside Al_2O_3 matrix when deposited in oxygen-free or oxygen-containing atmosphere, correspondingly. It is established that g-factor extracted from the FMR spectra of films with core–shell NPs decreases with x below the value g =2.0023 for free electron that is untypical for metallic NPs. This effect is associated with the formation of the interface between ferromagnetic core and *anti*ferromagnetic (ferrimagnetic) oxide shell of NPs.

1. Introduction

Nanocomposite M_x-I_{100-x} (20 at% ≤ x ≤ 80 at%) films containing NPs of 3D-metals (M=Fe, Co, Ni) or their alloys homogeneously distributed inside insulating matrixes (I=Al_2O_3, SiO_2, CaF_2) are actively studied due to their high-frequency applications in inductors, generators, sensors, transformers. It is well established that specified films possess versatile functional properties combining low coercive force (< 0.4 kA/m) and high electrical resistance (up to 10 Ω m) with excellent oxidation resistance, thermal and mechanical stability [1,2]. Particular interest is paid to the magnetic properties of nanocomposite film fabricated in oxygen-containing atmosphere when NPs with “metallic core – oxide shell” structure with medium diameter below 10 nm [3] are in superparamagnetic state at room temperature even at their very high concentrations (at x > 50 at%), i. e. above electric percolation threshold. Moreover, it is experimentally proved that deposition of films with core–shell NPs where oxide shell play the role of insulating barriers is the effective method of enhanced conductive and magnetoresistive properties [1–3].

Direct observation and control of core–shell structure of NPs in films by transmission electron microscopy is usually complicated because of extremely small thickness of oxide shells (below 1 nm [1]). In this paper we apply ferromagnetic resonance (FMR) spectroscopy for comparative analysis of magnetic properties of CoFeZr–Al_2O_3 films deposited in oxygen-containing atmosphere (oxidized films) and oxygen-free atmosphere (non-oxidized films) with respect to their structure and phase composition reported in [1–3]. As expected, variation of g-factors and demagnetizing fields B_d extracted from experimental FMR spectra for partially oxidized NPs will reflect and indirectly prove the formation of their core–shell structure.

2. Experimental

$(CoFeZr)_x(Al_2O_3)_{100-x}$ (31 at% ≤ x ≤ 47 at%) nanocomposite films with the thickness of 1 μm were deposited onto glass–ceramic substrates by d.c. ion sputtering of composite $Fe_{45}Co_{45}Zr_{10}$ alloy - amorphous Al_2O_3 target using 2 keV argon ion gun, at 0.28 nm/s. The base pressure in the chamber was 2.6×10^{-4} Pa, while the argon pressure equals to 6.7×10^{-2} Pa and oxygen pressure in case of reactive deposition was 4.2×10^{-3} Pa. Composition of the films was confirmed to be close to nominal by energy dispersive X-ray spectroscopy (EDX) [4]. Detailed and systematic analysis of $(CoFeZr)_x(Al_2O_3)_{100-x}$ (31 at% ≤ x ≤ 64 at%) films by X-ray diffraction, transmission electron microscopy,

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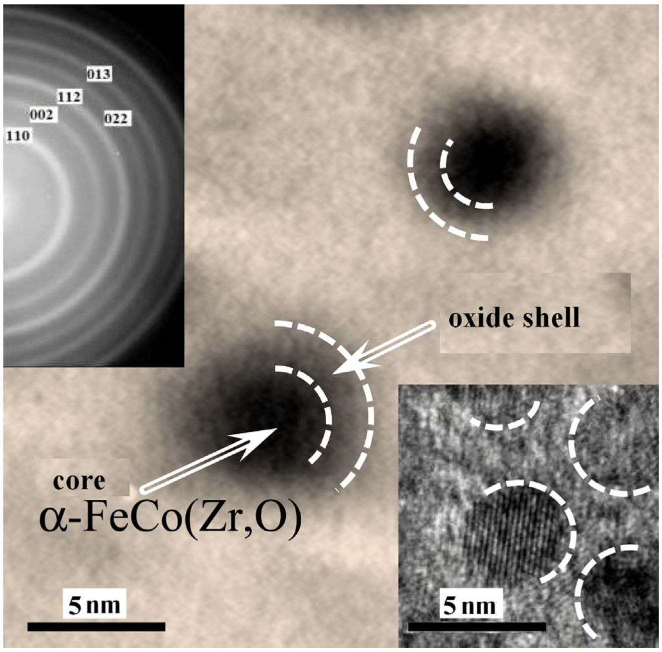

Fig. 1. Bright field TEM image taken from $(FeCoZr)_{36}(Al_2O_3)_{64}$ film illustrating a core–shell structure of NPs. The insets show selected area electron diffraction (on the top) and high resolution TEM image (in the bottom) of the film [2].

Mössbauer spectroscopy, X-ray absorption spectroscopy presented in [1–3] elucidated that films with $x \leq 50$ at% possess granular structure where NPs of bcc-FeCo alloy (for oxygen-free atmosphere) or "bcc-FeCo core – oxide shell" NPs (for oxygen-containing atmosphere) are homogeneously distributed inside Al_2O_3 matrix. Core–shell structure of NPs in films deposited in oxygen-containing atmosphere is illustrated in transmission electron microscopy (TEM) in Fig. 1. Composition of oxide shells was studied by X-ray absorption spectroscopy and low-temperature Mössbauer spectroscopy and identified as combination of $(Fe_xCo_{1-x})_{1-\delta}O$ and Fe^{3+}(Co)-based oxides, characterized with antiferro- or ferrimagnetic properties as evidenced by vibrating sample magnetometry [1].

In this paper magnetic properties of nanocomposite films were analyzed by FMR spectroscopy at room temperature using continuous wave X-band (microwave frequency f=9.32 GHz) electron spin resonance (ESR) spectrometer Varian E112 with modulation of magnetic field at f=100 kHz (the absorption signal is detected as its first derivative in the spectrum). Angular dependence of the induction of resonance field B_r was measured and analyzed to reveal magnetic anisotropy features of the films.

The orientation of samples in an external magnetic field B was characterized by the polar angle Θ_B (an angle between the normal vector of sample surface and the vector of magnetic induction of external field B) and by the azimuth ϕ (see Fig. 2). The θ_B values of 0° and 90°correspond to the perpendicular and parallel directions of B with respect to the films surface labeled hereinafter as OOP (out-of-plane) and IP (in-plane), correspondingly. The features of magnetic anisotropy were considered in terms of demagnetizing field B_d.

3. Results and discussion

FMR spectra of non-oxidized $(CoFeZr)_{31}(Al_2O_3)_{69}$ film recorded at $\theta_B = 0-90°$ are shown in Fig. 3. The spectra of all studied films are composed of a symmetric single line of typically 120 mT peak-to peak width evidencing homogeneous magnetization of films

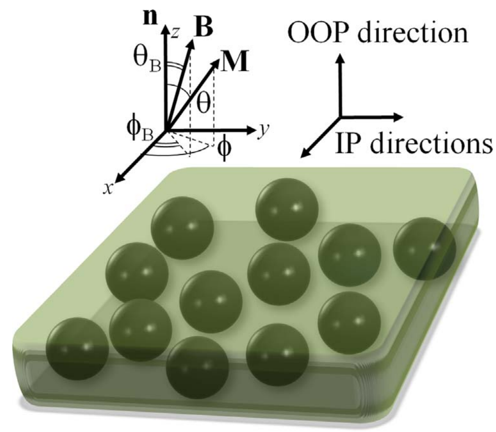

Fig. 2. The geometry of FMR measurements of nanocomposite films $(CoFeZr)_x(Al_2O_3)_{100-x}$ with a magnetic moment M in an external magnetic field with induction B.

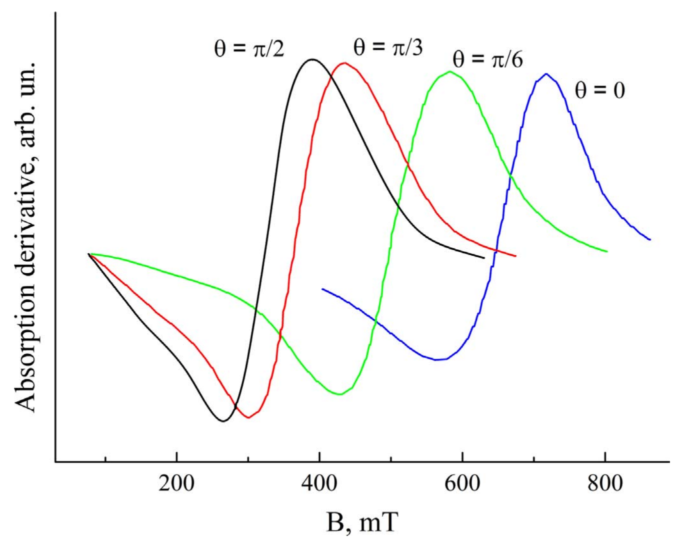

Fig. 3. FMR spectra of film $(CoFeZr)_{31}(Al_2O_3)_{69}$ sintered in oxygen-free atmosphere at different film's orientations in external magnetic field.

[5]. Values of B_r decreases with the increase of angle θ_B. Simultaneously, specified signals do not saturate with the increase of microwave power. These features of spectra indicate that resonance absorption in films is of ferromagnetic nature. It is noteworthy that in case of in-plane orientation of the samples the value of B_r remains constant for all angles ϕ, evidencing isotropic magnetic properties in the films plane.

The condition of resonance absorption of microwave radiation with frequency f in magnetic field B by a sample with magnetization M is defined by the energy dispersion relationship [6]:

$$\left(\frac{hf}{g\mu_B}\right)^2 = \left.\frac{\left(E_{\theta\theta}E_{\phi\phi} - E_{\theta\phi}^2\right)}{\left(M\cdot \text{Sin }\theta\right)^2}\right|_{\theta=\theta_0,\phi=\phi_0}, \quad (1)$$

where h – Planck constant, μ_B – Bohr magneton, M – the magnetization of a sample, $E_{\Theta\Theta}$, $E_{\phi\phi}$ and $E_{\Theta\phi}$ – the second derivatives of the sample free energy density E with respect to angles (θ, ϕ) of magnetization in spherical coordinate system (see Fig. 2) calculated at (θ_0, ϕ_0) corresponding to the equilibrium magnetization state. The equilibrium state of magnetization is defined by the condition of minimum of free energy density of the system: ($\partial E/\partial\theta = 0$, $\partial E/\partial\phi = 0$).

In case of uniformly magnetized films Landau – Lifshitz magnetization dynamics model is applicable [7]. Constant values of B_r