Julia KASIUK[1], Vadim BAEV[1], Julia FEDOTOVA[1], Vladimir SKURATOV[2], Vitalii BONDARIEV[3], Paweł ŻUKOWSKI[3], Tomasz N. KOŁTUNOVICZ[3]

National Centre for Particles and High Energy Physics of Belarusian State University (1), Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research (2), Department of Electrical Devices and High Voltage Technology, Lublin University of Technology (3)

doi:10.15199/48.2015.11.64

Characterization of ion-induced changes in magnetic anisotropy of FeCoZr-CaF_2 nanocomposite films by resonance methods

Abstract. *The paper is focused on the analysis of magneto-anisotropic properties of $(FeCoZr)_x(CaF_2)_{100-x}$ (x = 58 at.%, 73 at.%) nanocomposite films by Mössbauer and electron spin resonance spectroscopies. The studied films sputtered by ion-beam technique demonstrate perpendicular magnetic anisotropy (PMA) induced by the elongated shape of magnetic nanoparticles. Ion irradiation influence on PMA is studied depending on the treatment regimes. Ion fluence appropriate for desired PMA enhancement is defined as well as the possible reasons of such enhancement are discussed.*

Streszczenie. *Praca koncentruje się na analizie magneto-anizotropowych właściwościach warstwy granulowanego nanokompozytu $(FeCoZr)_x(CaF_2)_{100-x}$ (x = 58 at.%, 73 at.%) za pomocą spektroskopii Mössbauerowskiej oraz elektronowego rezonansu spinowego. W badanej warstwie, która była napylana za pomocą technik jonowych, zaobserwowano prostopadłą magnetyczną anizotropię (PMA) indukowaną przez wydłużony kształt nanocząsteczek magnetycznych. Zbadano wpływ napromieniowania jonami na PMA w zależności od trybu (typu) obróbki. Wyznaczono optymalne wartości fluensa dla zwiększenia efektu PMA, oraz omówiono możliwe przyczyny tego zwiększenia. (**Charakteryzacja jonowo indukowanych zmian anizotropii magnetycznej w nanokompozytowych warstwach FeCoZr-CaF_2 za pomocą metod rezonansowych**).*

Keywords: magnetic anisotropy, nanocomposites, resonance methods.
Słowa kluczowe: anizotropia magnetyczna, nanokompozyty, metody rezonansowe.

Introduction

Magnetic media with perpendicular anisotropy is of great practical interest because of the possibility of their application for high-density recording and high-resolution magnetic sensors designing [1]. Decrease in magnetic structures size required for devices compaction competes with the problem of supermagnetic limit. This problem can be successfully overcome by construction of the media with shape anisotropy of magnetic nanostructures. Thus, synthesis of metal-dielectric nanocomposite films with columnar structure of metallic phase allows blocking magnetic moments of metallic nanocolumns with only 4 nm in diameter [2] in the direction of columns axes. Additionally, conventional technique of ion-beam sputtering which is commonly used for nanocomposite films synthesis is the perspective way for making cheaper perpendicular magnetic media designing. Unfortunately, these materials can demonstrate deviations of magnetic moments orientation from films normal originating from such structural imperfections as dispersion of columns growth directions as well as irregularities of nanocolumns size and distribution inside the matrix [2, 3]. Such defects decreases the effect of perpendicular magnetic anisotropy (PMA) and breaks the homogeneity of magnetic nanostructures distribution. Additional treatment eliminating structural imperfections is demanded. The irradiation of FeCoZr-CaF_2 films with PMA by high-energy heavy ions was proposed. Highly-disordered thin channels (1-5 nm) formed in material in the result of such treatment are aimed at PMA enhancement by homogenization of nanocolumns orientations along the ion flux direction.

Experimental

The films $(FeCoZr)_x(CaF_2)_{100-x}$ (x = 58 at.%, 73 at.%) were synthesized by ion-beam sputtering technique on Al substrates in Ar atmosphere. Irradiation was carried out by 167 MeV Xe^{26+} ions with fluence D in the range 7×10^{12} – 10^{13} ion/cm^2 generated by IC-100 heavy ion cyclic accelerator (JINR, Dubna). Ion beam was orientated along the normal to the films plane.

The ^{57}Fe Mössbauer spectra were obtained in the transmission geometry using 40 mCi ^{57}Co/Rh source at room temperature. The spectra were analyzed with MOSMOD software based on the method published in [4]. Magnetic resonance spectra were measured at room temperature using continuous wave X-band (microwave frequency 9.32 GHz) electron spin resonance (ESR) spectrometer Varian E112 with modulation of magnetic field at frequency 100 kHz. The absorption signal is detected as its first derivative in the spectrum.

Results and Discussion

Mössbauer spectra of $(FeCoZr)_{58}(CaF_2)_{42}$ nanocomposite films are presented in Fig.1. Initial film spectrum (Fig.1a) consists of dominating magnetically split sextet corresponding to α-FeCo(Zr) phase [2, 3] showing ferromagnetic ordering. Small additional doublet characterizing α-FeCo(Zr) phase in superparamagnetic (SP) state probably attributes to small nanoparticles indicating particles size dispersion. The sextet demonstrates specific relative intensities of spectral lines such as $h1{:}h2{:}h3$ = 3:0.52:1 (Fig.1a) indicating preferential orientation of nanoparticles magnetic moments in the direction close to the film normal. The average angle θ between magnetic moments and the film normal calculated in accordance with relation θ = arcos $[(4\text{-}K)/(4+K)]1/2$, $K = h2/h3$, [2] is equal to 29º. Study of the sample cross-section by transmission electron microscopy [2] shows columnar-like structure of metallic nanoparticles which are elongated in the film normal direction. Detected deviation θ can be associated with some dispersion of columns growth directions.

Mössbauer spectrum of (FeCoZr)58(CaF2)42 film irradiated with fluence $D = 7\cdot10^{12}$ ion/cm^2 is presented in Fig.2b. It demonstrates considerably narrower spectral lines of sextet than in the case of initial film which is evidencing better ferromagnetic ordering probably originating from crystalline arrangement. Additionally, broad singlet line appears which corresponds to oxide or fluoride phase in accordance with its isomer shift (δ = 0.36 mm/s). Sextet lines intensities relation is 3:0.80:1 that corresponds to θ = 35º.

Irradiation of the film with $D = 10^{13}$ ion/cm^2 leads on the contrary to the sextet lines broadening, whereas θ

decreases to 24º (see Fig.1c). The latter indicates the enhancement of PMA as compared to the initial film. Sextet broadening is the result of some structural disordering in α-FeCo(Zr) phase after irradiation with high fluence.

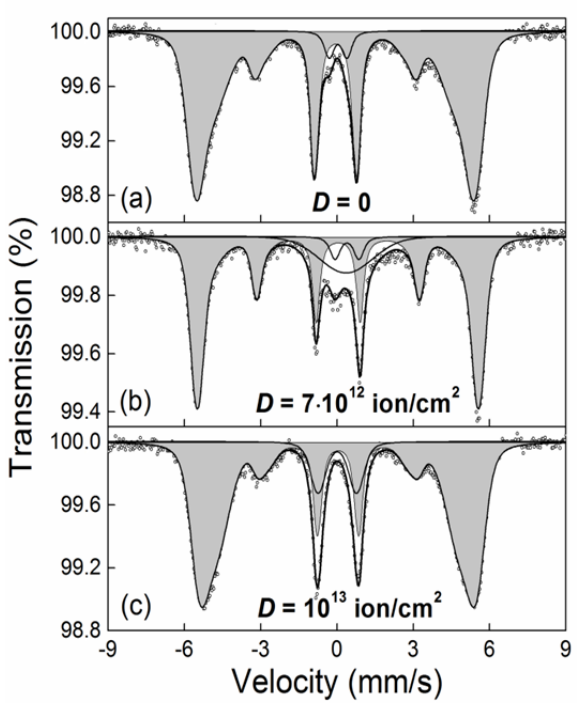

Fig.1. Mössbauer spectra of $(FeCoZr)_{58}(CaF_2)_{42}$ films – initial (*a*) as well as irradiated with fluences $D = 7 \cdot 10^{12}$ ion/cm^2 (*b*) and $D = 1 \cdot 10^{13}$ ion/cm^2 (*c*)

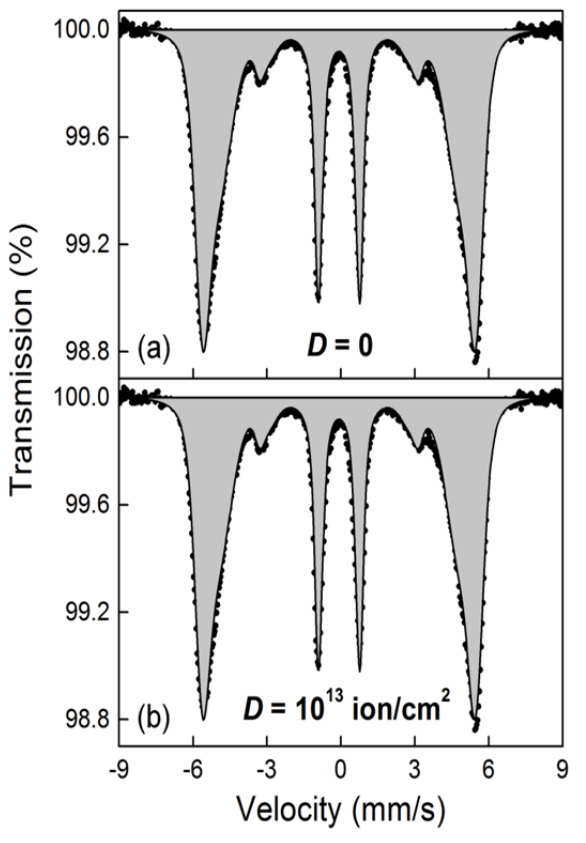

Fig.2. Mössbauer spectra of $(FeCoZr)_{73}(CaF_2)_{27}$ films – initial (*a*) and irradiated with fluence $D = 1 \cdot 10^{13}$ ion/cm^2 (*b*)

Mössbauer spectra of $(FeCoZr)_{73}(CaF_2)_{27}$ nanocomposite films presented in Fig.2 consist only of sextet corresponding to ferromagnetically ordered α-FeCo(Zr) nanoparticles. Analysis of Fe local states in the film after irradiation with $D = 10^{13}$ ion/cm^2 also shows some PMA enhancement according to the relative line intensities (Fig.2b), similarly to the case of $(FeCoZr)_{58}(CaF_2)_{42}$ sample irradiated with the same dose. However the decrease of θ is low (from 24º for initial film to 21º).

The peculiarities of magnetic anisotropy of nanocomposite films were additionally analyzed by ESR spectroscopy. The orientation of samples in an external magnetic field was characterized by the polar angle θ_B (an angle between the normal to the sample plane and the magnetic external field B). Zero θ_B value corresponds to the direction of the field perpendicular to the sample surface and is labeled below as OP (out-of-plane). Similarly the direction of the field parallel to the sample surface $\theta_B = 90°$) is labeled as IP (in-plane). The peculiarities of magnetic anisotropy are discussed in terms of components of demagnetizing factors tensor NIP and NOP.

ESR spectra of initial $(FeCoZr)_{58}(CaF_2)_{42}$ film and the film irradiated with $D = 10^{13}$ ion/cm^2 are shown in Fig.3 for both orientations of external magnetic field. Spectra signals represent wide intense single lines. The value of resonance magnetic field B_r depends on angle θ_B. Resonance signals are not saturated with microwave power increase. These pecularitiy of spectra indicates that the microwave absorption is caused by ferromagnetic resonance (FMR).

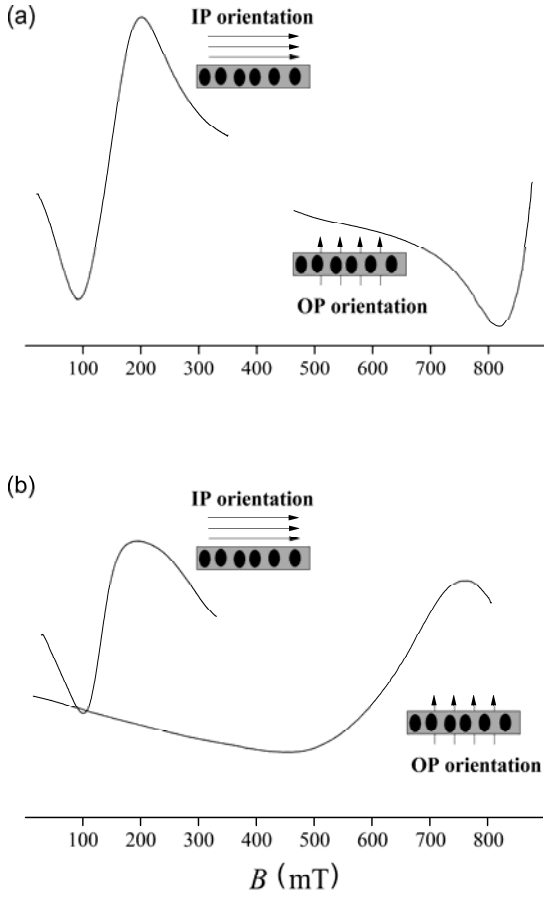

Fig.3. Magnetic resonance spectra of initial (*a*) and irradiated with $D = 10^{13}$ ion/cm^2 (*b*) $(FeCoZr)_{58}(CaF_2)_{42}$ films measured at different orientations of external magnetic field

Numerical analysis of FMR spectra using for g-factor, N_{IP} and N_{OP} calculations is based on Landau – Lifshitz model of magnetization dynamics and the energy dispersion relationship [5] as well as the Smit-Beljers-Suhl formula for a resonance condition [6]. The dependence of a resonance condition on orientation of the sample in external field is expressed as:

$$(hf/g\mu_B)^2 = \left[B_r\mathrm{Cos}(\theta_B - \theta) + B_d\mathrm{Cos}(2\theta)\right]\cdot \left[B_r\mathrm{Cos}(\theta_B - \theta) + B_d\mathrm{Cos}^2(\theta)\right] \quad (1)$$

where: h – Planck constant, f – microwave frequency, μ_B – Bohr magneton, B_r – the value of resonant magnetic field, θ_B and θ – the polar angles between the normal to the sample surface and the external field B, B_d – demagnetizing field caused by the shape anisotropy of magnetic sample.

The demagnetizing field B_d is proportional to magnetization of the sample and is defined by components of demagnetizing factors tensor. In the case of an isotropic film, B_d can be characterized in terms of two components of demagnetizing factors tensor – N_{IP} and N_{OP} which correspond to in-plane and out-of-plane directions [7]:

$$B_d = \mu_0(N_{IP} - N_{OP})M. \quad (2)$$

It should be noted that demagnetizing tensor is normalized to unity, so $2\cdot N_{IP} + N_{OOP} = 1$.

Using the values of B_r at two perpendicular orientations $\theta_B = 0°$ and $\theta_B = 90°$ (B_{OP} and B_{IP}, respectively) g-factor and demagnetizing field B_d can be calculated (see Table 1). Basing on the value B_d one can easely determine the N_{IP} and N_{OP} values for the samples. Also it is possible to calculate the values of demagnetizing factors N_{IP}^{gr} и N_{OP}^{gr} of a single granule averaged over the volume of the sample using the expression:

$$(N_{IP} - N_{OP}) = (N_{IP}^{gr} - N_{OP}^{gr})(1 - f_V)/f_V - 1, \quad (3)$$

where: f_V – volume filling factor of granules in nanocomposite film.

Calculated values of demagnetizing factors N_{IP} and N_{OP} of all studied films (Table 1) indicates that the films easy magnetization direction lies in the films plane (easy plane anisotropy, $N_{OP} > N_{IP}$) [7]. However, basing on calculated values of single granule demagnetizing factors N_{IP}^{gr} и N_{OP}^{gr} (see Table 1) one can conclude that nanoparticles in all films studied possess elongated shape, and their easy magnetization direction corresponds to nanoparticles long axis (easy axis anisotropy) oriented perpendicularly to the sample surface. This confirms the result of Mössbauer spectroscopy finding out PMA in the films.

Table 1. The values of demagnetizing field B_d and demagnetizing factors N (in plane N_{IP} and out of films plane N_{OP}) for nanocomposite films $(FeCoZr)_x(CaF_2)_{100-x}$ (x = 58 at.%, 73 at.%) and average single granule (N_{IP}^{gr} and N_{OP}^{gr}) calculated basing on ESR spectroscopy results

x, at.%	D, ion/cm^2	B_d, mT	N of sample		N of granule	
			$2\cdot N_{IP}$	N_{OP}	$2\cdot N_{IP}^{gr}$	N_{OP}^{gr}
58	0	-610	0.13	0.87	0.78	0.22
	$7\cdot10^{12}$	-481	0.25	0.75	0.88	0.12
	$1\cdot10^{13}$	-500	0.23	0.77	0.86	0.14
73	0	-586	0.27	0.73	1	0
	$8\cdot10^{12}$	-489	0.33	0.67	1	0
	$1\cdot10^{13}$	-677	0.21	0.79	0.96	0.04

Using calculaded values of demagnetizing factors of elongated ellipsoid modeling the shape of magnetic nanoparticles, it is possible to estimate the ratio of ellipsoid axis for a single granule averaged over the volume of the sample [7]. Thus, in initial $(FeCoZr)_{58}(CaF_2)_{42}$ film, nanoparticles aspect ratio is ~1.2:1 that corresponds to weakly elongated magnetic structures. After irradiation under both conditions it modifies to ~3:1 denoting significantly more evident particles elongation and the increase of perpendicular contribution in magnetic anisotropy. PMA enhancement after irradiation detected both Mössbauer and ESR spectroscopy possibly originates from alignment of magnetic nanoparticles orientations by perpendicularly oriented ion tracks. They "cut" nanoparticles whose growth direction deviates from film normal and form additional non-magnetic barriers between α-FeCo(Zr) nanocolumns preventing their magnetic interaction.

In case of the $(FeCoZr)_{73}(CaF_2)_{27}$ nanocomposite films the values of demagnetizing factors of a single granule (Table 1) indicate that the shape of column-like nanoparticles is close to infinite cylinder, both before and after irradiation.

Conclusions

Use of combination of complimentary techniques, namely Mössbauer and electron spin resonance spectroscopies, for analysis of magnetic state of nanocomposite films makes it possible to detect magnetic anisotropy changes in films as the result of their irradiation by heavy ions. It is established that initial $(FeCoZr)_x(CaF_2)_{100-x}$ (x = 58 at.%, 73 at.%) films are characterized by preferential orientation of nanoparticles magnetic moments close to the films normal (PMA) and elongated shape of averaged magnetic nanoparticles varying from elongated ellipsoid for x = 58 film to infinite cylinder for x = 73 sample. Irradiation of the studied films demonstrating PMA by Xe ions with fluences D = 7-10·10^{12} ion/cm2 leads to the decrease of the angle θ characterizing deviations of nanoparticles magnetic moments from films normal from 24-29° for initial films to 21-24° as well as elongation of magnetic nanoparticles shape.

We acknowledge the support from the project F14M-029 of Belarusian Foundation for Fundamental Research and the Belarusian State program "Functional materials", project 1.37.

This study was partly carried out in the framework of the research project No IP 2012 026572 within the Iuventus Plus program of the Polish Ministry of Science and Higher Education in the years 2013–2015.

Special gratitude to Prof. Yu. Kalinin and Dr. hab. A. Sitnikov for providing the samples synthesis.

REFERENCES

[1] Sun S., Murray C.B., Weller D., Folks L., Moser A., Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices, Science, 287 (2000), n.5460, 1989-1992

[2] Kasiuk J.V., Fedotova J.A., Przewoznik J., Zukrowski J., Sikora M., Kapusta Cz., Grce A., Milosavljevic M., Growth-induced non-planar magnetic anisotropy in FeCoZr-CaF_2 nanogranular films: Structural and magnetic characterization, Journal of Applied Physics, 116 (2014), 044301

[3] Kasiuk J.V., Fedotova J.A., Koltunowicz T.N., Zukowski P., Saad A.M., Przewoznik J., Kapusta Cz., Zukrowski J., Svito I.A., Correlation between Local Fe States and Magnetoresistivity in Granular Films Containing FeCoZr Nanoparticles embedded into Oxygen-free Dielectric Matrix, Journal of Alloys and Compounds, 586 (2014), Supplement 1, S432-S435

[4] Rancourt D.G, Ping J.Y., Voight-based methods for arbitrary-shape static hyperfine parameter distribution in Mössbauer spectroscopy, Nuclear Instruments and Methods in Physics Research Section B 58 (1991), 85-97

[5] Landau L.D., Lifshits E.M., Electrodynamics of Continuous Media, 2nd edition, Oxford, England: Pergamon Press, 1984
[6] Suhl H., Ferromagnetic Resonance in Nickel Ferrite Between One and Two Kilomegacycles, Physical Review 97 (1955), n.2, 555
[7] Cullity B.D., Graham C.D., Introduction to Magnetic Materials. John Wiley & Sons: IEEE Press, Hoboken, New Jersey 2009, 544 p.

***Authors**: Ph.D. Julia Kasiuk, National Centre for Particles and High Energy Physics of Belarusian State University, 153, Bogdanovich Str., 220040 Minsk, Belarus; Ph.D. Vadim Baev, National Centre for Particles and High Energy Physics of Belarusian State University, 153, Bogdanovich Str., 220040 Minsk, Belarus; Prof. Julia Fedotova, National Centre for Particles and High Energy Physics of Belarusian State University, 153, Bogdanovich Str., 220040 Minsk, Belarus, julia@hep.by; Prof. Vladimir Skuratov, Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions, Joliot-Curie 6, 141980 Dubna, Moscow Region, Russia; M.Sc. Vitalii Bondariev, Department of Electrical Devices and High Voltages Technologies, Lublin University of Technology, Nadbystrzycka 38a, 20-618 Lublin, Poland; Prof. Paweł Żukowski, Department of Electrical Devices and High Voltages Technologies, Lublin University of Technology, Nadbystrzycka 38a, 20-618 Lublin, Poland, E-mail: p.zhukowski@pollub.pl; Ph.D. Tomasz N. Koltunowicz, Department of Electrical Devices and High Voltages Technologies, Lublin University of Technology, Nadbystrzycka 38a, 20-618 Lublin, Poland, E-mail: t.koltunowicz@pollub.pl.*