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Dielectric Properties of $(\mathrm{CoFeZr})_x(\mathrm{PZT})_{100-x}$ Nanocomposites Produced with a Beam of Argon and Oxygen Ions

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In this paper it was established that nanocomposite $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$, with $x = 90.0$ at.%, produced by ion sputtering with argon and oxygen beam remains under the percolation threshold. It is related to the compound structure of films and creation of coat consisting of metallic oxides on surface of metallic phase nanogranules, which prevents electric contact between nanoparticles. Verification of the Arrhenius dependences for capacity and conductivity demonstrates that dominant part of metallic phase nanogranules has metal oxide coatings. Only a small number of nanogranules (probably around a few percent) does not have oxide coating.

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1. Introduction

Preparation, production, and examination of new magnetic and magnetoresistive nanomaterials and structures based on them is one of the most interesting and prospective direction in materials engineering. Topical interest in this research area is related to the fact that these materials have structure and phase composition on nanodimensional level, which causes occurrence of physical-chemical properties, which are very different from properties of materials with dimensions in micro and millimetres [1]. It is necessary to mention interesting magnetic properties [2, 3], particularly magnetotransport properties — magnetoresistive tunnelling phenomena [4]. These materials have also higher values of many mechanical properties, for example microhardness and tribological properties [5]. Causes of differences in properties of nanocomposites and bulk materials are growing impact of surface (surface energy) with transit of granules into nanodimensions and impact, in many cases, of quantum-dimensions effects [1].

From a wide range of nanomaterials and nanostructures, special place is taken by soft magnetic grain materials, which consist of nanoparticles of ferromagnetic alloy distributed in dielectric or ferroelectric matrix [6, 7]. These materials can be used in magnetoelectronics, including spintronics, in structure of sensors of electric, magnetic and non-electric values, and in many different uses [8].

For examination there were chosen nanocomposites with metal–dielectric structure of composition $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$ where ferroelectric phase PZT is an acronym for first letters of main elements of matrix — $(\mathrm{Pb}_{81}\mathrm{Sr}_4(\mathrm{Na}_{50}\mathrm{Bi}_{50})_{15}(\mathrm{Zr}_{57.5}\mathrm{Ti}_{42.5}))\mathrm{O}_3$. Films were prepared by ion sputtering of metal–dielectric targets with argon and oxygen ions beam.

2. Experimental

Nanocomposites were prepared according to method described in paper [9] for sputtering ion-argon beams (non-oxygen films) or mixed argon and oxygen ions (oxygen films) were used. Examination of AC electric properties (resistance and capacity in equivalent parallel circuit, and phase shift angle and loss tangent) were made using measurement state described in paper [10]. Measurement range of frequencies amounted to 50 Hz–5 MHz. Due to occurrence of large errors at the end of the measurement range, results over 1 MHz were not considered for the analysis. Measurements were carried out within the temperatures range from 77 K to 373 K with 5 K step. In this paper 15 min annealing in a tubular furnace was used within the temperature range from 398 K and higher and with the 25 K step.

3. Results and discussion

The paper presents results of examination of $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$ film with very high content of metallic phase, amounting to 90.0 at.%. In case of less complex matrixes, for example $(\mathrm{FeCoZr})_x(\mathrm{Al_2O_3})_{100-x}$, percolation threshold of nanocomposites, which were sputtered with pure argon ions beam, amounts to around (54 ± 2) at.% [11], and percolation threshold for nanocomposites sputtered with mixed argon and oxygen ions beam increases to value of around (78 ± 5) at.% [12].

Figure 1 shows the Arrhenius dependences on conductivity of films annealed in temperatures from 398 K to 548 K. As is shown in this figure, derivative conductivity values from the temperature amounts to

$$\frac{\mathrm{d}\sigma}{\mathrm{d}T} > 0. \qquad (1)$$

This means that nanocomposite $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$ with $x = 90.0$ at.% remains under the percolation threshold. It is probably connected with the compound structure of examined films and, similarly to oxygen matrix $\mathrm{Al_2O_3}$, creation of metal oxides on surface of metallic phase nanogranules, which prevents electric contact be-

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tween nanoparticles. It is also confirmed by low value of conductivity of film with $x = 90.0$ at.%, which amounts in low temperatures from about 7×10^{-5} Ω^{-1} cm^{-1} (Fig. 1). For comparison, thin film of sheer ferromagnetic alloy, obtained by ion sputtering, has conductivity of approximately 2.7×10^{3} Ω^{-1} cm^{-1}, that is approximately 3×10^{7} times higher than nanocomposite film.

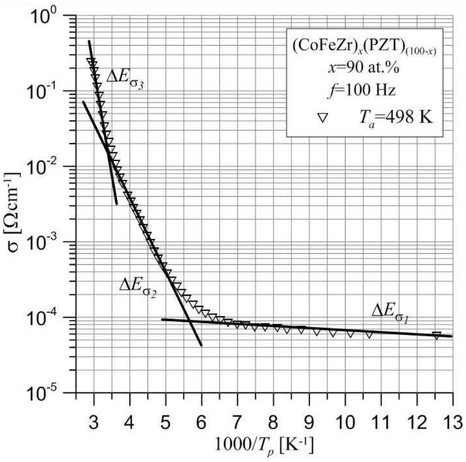

Fig. 1. Arrhenius dependences on conductivity for nanocomposite $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$ with $x = 90.0$ at.%, annealed in temperature 498 K, measurement frequency 100 Hz.

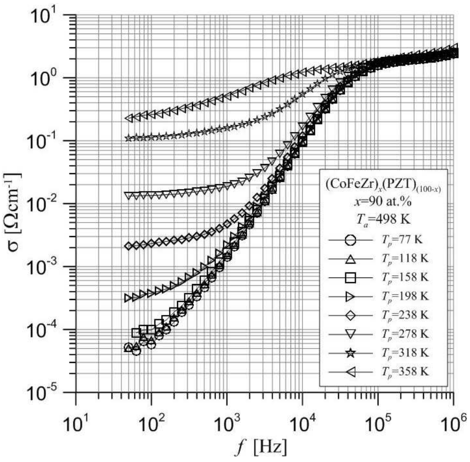

Fig. 2. Frequency dependences on conductivity for nanocomposite $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$ with $x = 90.0$ at.%, annealed in temperature 498 K for different measurement temperatures.

Figure 2 shows frequency dependences on conductivity for selected measurement temperatures. As it can be seen, strong frequency dependences occur, causing conductivity increase from three to four orders of magnitude, depending on measurement temperature. According to [13] occurrence in the material of frequency dependence on conductivity proves the hopping mechanism of conduction. It is easily understandable if it is taken into consideration that metallic phase nanoparticles are separated by dielectric layer of high resistivity. This means that during current flow carriers have to go through insulating barriers which separate metallic phase nanoparticles. It is possible only by electron tunnelling.

An interesting fact is that in areas of low and high measurement frequencies values of conductivity σ_{L} and σ_{H} are almost independent of frequency (see Fig. 2). These conductivity dependences can be explained by use of model of hopping conductance on AC and DC, presented in papers [14, 15]. Model predicts that after electron tunnelling from one neutral potential well created by metallic phase nanoparticle to another a dipole appears, therefore, increase of dielectric permittivity takes place. After dipole life τ electron with probability p can make another jump in direction opposite to electric field (DC) or come back with probability $1-p$ to the positively charged well (AC, dipole disappearance). From, obtained on the basis of model, equation for real component of alternating current density (conductivity) it results that values of conductivity in low and high frequency areas are independent of frequency, as shown in Fig. 2. In the frequencies transition region model predicts increase of conductivity. Quotient of low-frequency conductivity and high-frequency conductivity equals value of probability of the jump p:

$$\frac{\sigma_{\mathrm{L}}}{\sigma_{\mathrm{H}}} = p. \qquad (2)$$

In Fig. 3 frequency dependences of capacity of examined films are presented. As can be seen, in the area of low and middle frequencies $C_p = \text{const}$, and with further growth of frequency, when

$$\frac{1}{2\pi f} < \tau, \qquad (3)$$

capacity value C_p decreases. As it is evident from Fig. 3, for measurement temperatures around 250 K capacity characteristic is almost independent of temperature.

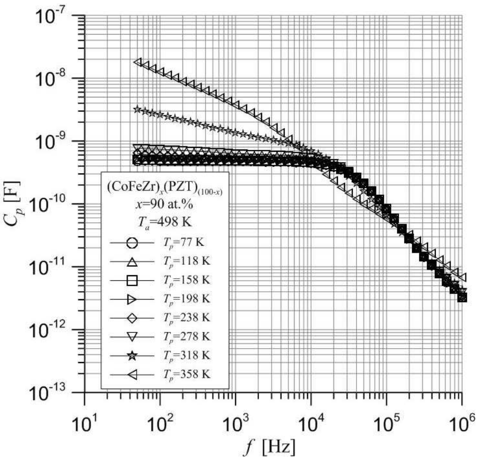

Fig. 3. Frequency dependences on capacity for nanocomposite $(\mathrm{FeCoZr})_x(\mathrm{PZT})_{100-x}$ with $x = 90.0$ at.%, annealed in temperature 498 K for different measurement temperatures.

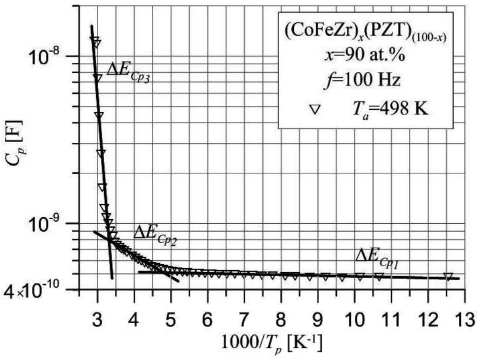

Fig. 4. Arrhenius dependences on capacity for nanocomposite $(FeCoZr)_x(PZT)_{100-x}$ with $x = 90.0$ at.%, annealed in temperature 498 K, measurement frequency 100 Hz.

Figure 4 presents Arrhenius dependences for capacity. As shown in this figure, over temperature 250 K heavy increase of capacity takes place. It is accompanied by almost ten times increase of low-frequency activation energy of capacity, measured on frequency 100 Hz, from value of around 0.002 eV to around 0.03 eV. In higher temperatures activation energy of capacity increases to value of around 0.5 eV. This means that in examined nanofilms there appear at least two types of potential wells created by nanoparticles of metallic phase. Because of high content of metallic phase (90.0 at.%) some of nanoparticles can have unoxidized surface, whereas the rest can have coating from oxides of metal atoms of metallic phase. Such coating creates potential barrier, which increases activation energy of electron hopping, causing creation of dipoles. Going through additional barrier demands higher measurement temperatures.

In case of above mentioned types of potential wells, the following jumps can appear:

- well without coating — well without coating, activation energy ΔE_{C1} the lowest;
- well with coating — well without coating, activation energy ΔE_{C2} higher than previous one;
- well with coating — well with coating, activation energy ΔE_{C3} the highest.

Similar situation takes place also for activation energy of conductivity, which is shown in Fig. 1. As Fig. 4 presents, above temperature 250 K, where jumping between particles takes place, capacity increases almost 50 times. It means that only small number of nanoparticles of the metallic phase (probably around a few percent) does not have oxide coating. Remaining nanoparticles have coatings, which consist of oxides of metallic phase atoms.

4. Resume

It was established that nanocomposite $(FeCoZr)_x(PZT)_{100-x}$ with $x = 90.0$ at.% produced by sputtering with argon and oxygen ions remains under the percolation threshold. It is related to complex structure of examined films and with creation of layer of metal oxides on the surface of metallic phase nanogranules, which prevents electric contact between nanoparticles. From the analysis of the Arrhenius dependences for capacity and conductivity it appears that dominant part of nanogranules of metallic phase has metal oxides coating. Only small number of nanogranules (probably around a few percent) does not have oxide coating.

Acknowledgments

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