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Annealing of $(CoFeZr)_x(CaF_2)_{100-x}$ Nanocomposites Produced by the Ion-Beam Sputtering in the Ar and O_2 Ambient

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This paper presents the investigations of electrical properties and effect of annealing on conductivity of $(CoFeZr)_x(CaF_2)_{100-x}$ nanocomposites produced by ion-beam sputtering in the Ar and O_2 ambient. Investigations into conductivity of $(CoFeZr)_x(CaF_2)_{100-x}$ nanocomposites depending on the measuring temperature and the annealing temperature have been performed. The application of a combined argon–oxygen beam brings about lowering of the potential barrier on the surface of nanoparticles. In the course of annealing the additional oxidation occurs. First it proceeds on the surface and then all through the metallic-phase particles.

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1. Introduction

Our previous research projects concerned testing of structural, electrical and magnetic properties of nanocomposites $(CoFeZr)_x(Al_2O_3)_{100-x}$ and $(CoFeZr)_x(PZT)_{100-x}$ produced by ion sputtering with a beam of pure argon or a mixture of argon and oxygen [1–5]. It has been found that the electrical and magnetic properties are influenced by the presence of oxygen. As early as in the course of the nanocomposite formation by the beam of argon and oxygen ions, that a layer of oxides of the metallic-phase metals forms on the surface of the nanoparticles [6]. It causes shifting of the percolation threshold to the area of higher metallic-phase contents x from 54 at.% for a beam of pure argon [3] up to 78 at.% for a beam of argon and oxygen [7]. Annealing in the atmospheric air can have intensifying effect on the mentioned phenomena as it causes diffusion of oxygen into the nanocomposite film. The process leads to further oxidation of the metallic-phase nanoparticles and to changes in electrical properties of the nanocomposites $(CoFeZr)_x(Al_2O_3)_{100-x}$ [8, 9].

The dielectric Al_2O_3 has been applied to the testing. In the course of the sputtering process it can release oxygen atoms and thereby contribute to partial oxidation of the nanoparticle surfaces even when a beam of pure argon is applied to the sputtering.

The paper presents an analysis of electrical properties of $(CoFeZr)_x(CaF_2)_{100-x}$ nanocomposites produced by means of ion sputtering with a beam of argon and oxygen illustrated by using a sample of the metallic-phase content of $x = 72.5$ at.% — considerably exceeding the percolation threshold $x_C \approx 50$ at.% of binary metal-dielectric nanocomposites [10].

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2. Experimental results and discussion

Figure 1 presents the frequency dependences of conductivity of a non-annealed $(CoFeZr)_x(CaF_2)_{100-x}$ film for six selected temperatures contained within the range from the liquid nitrogen temperature (LNT) up to the room temperature (RT). As can be seen in the figure, within the low-frequency area the conductivity value is constant $\sigma(f) \approx$ const. Close to the frequency of 10^4 Hz an increase of the σ value can be observed, still tending to be constant.

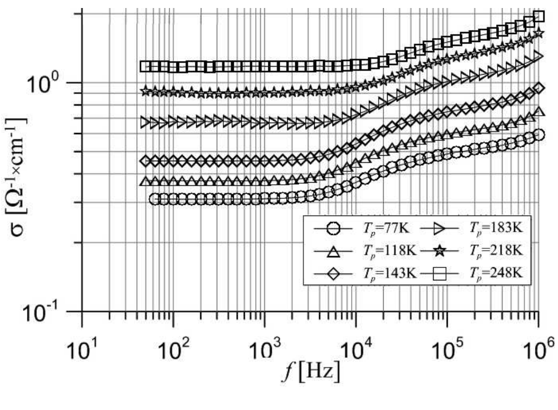

Fig. 1. Frequency vs. the conductivity σ of the non-annealed nanocomposite $(CoFeZr)_{72.5}(CaF_2)_{27.5}$ for selected measuring temperatures T_p.

The increase of σ along with the frequency increase indicates a hopping mechanism of charge conductivity in the nanocomposite. A model of that phenomenon has been elaborated and verified in [11–13].

In order to determine basic parameters of hopping recharging such as the time lapse between the sequent jumps $\tau \approx 1/2\pi f_{\max}$ (see Fig. 2), probability of jumps and others, in [11] a notion of frequency coefficient α has been introduced

$$\alpha = \frac{\mathrm{d}\,(\lg \sigma)}{\mathrm{d}\,(\lg f)}. \tag{1}$$

Diagrams of the coefficient α for a non-annealed sample are presented in Fig. 2. It can be seen in the figure that in a non-annealed sample two mechanisms of hopping recharging with the time value of $\tau \approx 5 \times 10^{-6}$ s can be observed.

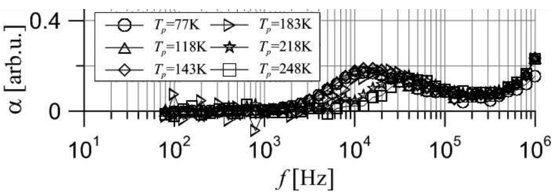

Fig. 2. Frequency vs. the frequency coefficient α of the non-annealed nanocomposite $(\mathrm{CoFeZr})_{72.5}(\mathrm{CaF_2})_{27.5}$ for selected measuring temperatures T_{p}.

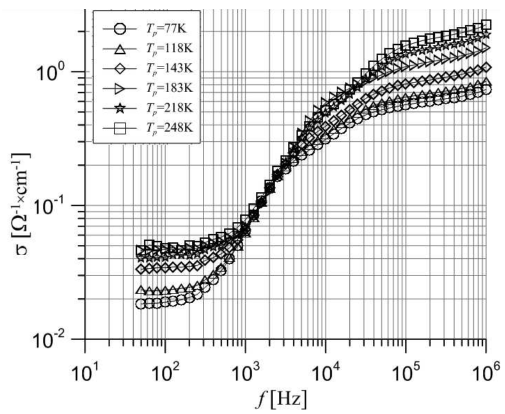

Fig. 3. Frequency vs. the conductivity σ of the nanocomposite $(\mathrm{CoFeZr})_{72.5}(\mathrm{CaF_2})_{27.5}$ annealed at the temperature of $T_{\mathrm{a}} = 448$ K for selected measuring temperatures T_{p}.

Annealing at $T_{\mathrm{a}} = 448$ K of the 15 min duration causes the occurrence of two maxima and their shift to the area of lower frequency (Figs. 3 and 4). The first maximum is characterized by the time value of $\tau_1 \approx 1.6 \times 10^{-4}$ s and the other of $\tau_2 \approx 8 \times 10^{-6}$ s. In our opinion, the shift is related to the diffusion of a small amount of metal atoms that have been trapped in the dielectric matrix during the film deposition process and their joining of the metallic-phase nanoparticles. A similar phenomenon has been observed in [14]. The atoms have shortened their jumping path between the metallic-phase nanoparticles and consequently, the time lapse τ between the sequent jumps as well. The presence of two maxima can be also seen at higher annealing temperatures e.g. at $T_{\mathrm{a}} = 598$ K

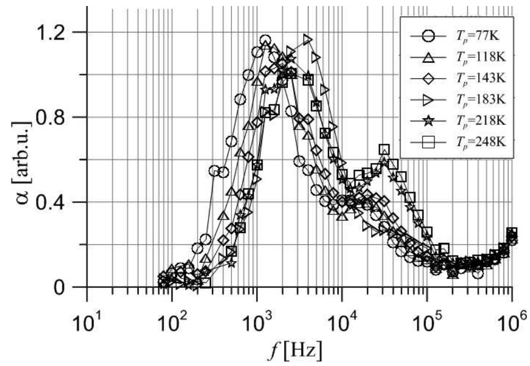

Fig. 4. Frequency vs. the frequency coefficient α of the nanocomposite $(\mathrm{CoFeZr})_{72.5}(\mathrm{CaF_2})_{27.5}$ annealed at the temperature of $T_{\mathrm{a}} = 448$ K for selected measuring temperatures T_{p}.

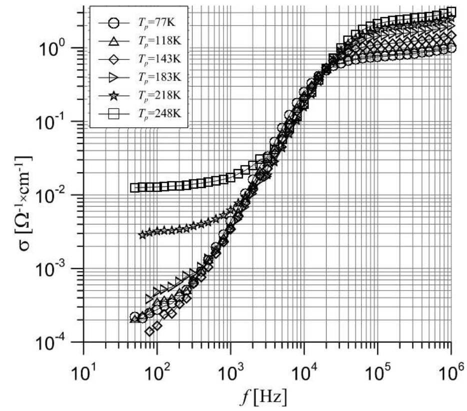

Fig. 5. Frequency vs. the conductivity σ of the nanocomposite $(\mathrm{CoFeZr})_{72.5}(\mathrm{CaF_2})_{27.5}$ annealed at the temperature of $T_{\mathrm{a}} = 598$ K for selected measuring temperatures T_{p}.

(Figs. 5 and 6). At low measuring temperatures one wide maximum $\alpha(f)$ occurs — Fig. 6. It results from overlapping of two maxima that differ from each other by the τ values. When the measuring temperature gets increased up to $T_{\mathrm{p}} = 218$ K, the maximum of the lower-frequency area vanishes and one narrow maximum of $f_{\max} \approx 10^4$ Hz is left.

Aside with the time τ value there is another important parameter of the hopping recharging process and it is the maximum value of the frequency coefficient $\alpha_{\max}$, which can be determined on the basis of diagrams shown in Figs. 2, 4 and 6. According to [15] in the case of tunneling $\alpha \le 0.8$. Higher values can indicate the occurrence of jumps over the potential barrier.

Figure 7 presents the dependences $\alpha_{\max}$ vs. annealing temperatures T_{a}, obtained at selected room temperatures. As can be seen in the figure, up to the $T_{\mathrm{a}} = 423$ K the $\alpha_{\max}$ value remains at the level that is much lower than 0.8. It can indicate that the conductivity is realized over the metal atoms that are trapped in the dielectric matrix. Their diffusion towards the metallic-phase nanoparticles causes an increase of $\alpha_{\max}$ at $T_{\mathrm{a}} = 448$ K

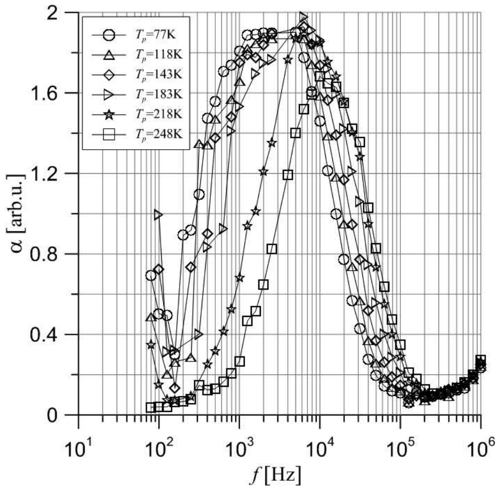

Fig. 6. Frequency vs. the frequency coefficient α of the nanocomposite $(CoFeZr)_{72.5}(CaF_2)_{27.5}$ annealed at the temperature of $T_a = 598$ K for selected measuring temperatures T_p.

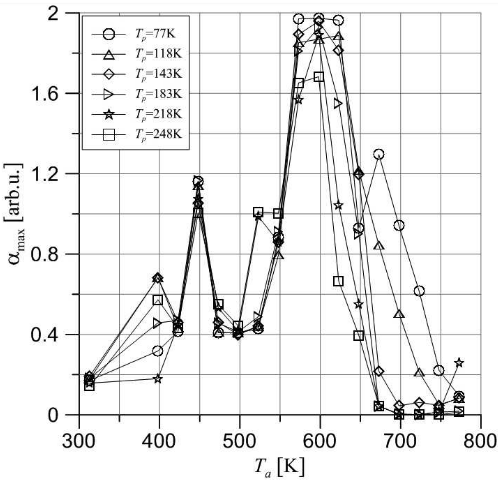

Fig. 7. Maximum value of the frequency coefficient α_{max} vs. the annealing temperature T_a for selected measuring temperatures T_p.

as well as over ten-times lower conductivity at the LNT (Fig. 3) as compared with a non-annealed sample (Fig. 1). In our opinion, the α_{max} value increases resulting from the annealing at temperatures of 548 K and higher can be related to the oxidation of the metallic-phase nanoparticle surfaces during the diffusion of oxygen from air.

Lower values of the α_{max} at the annealing temperatures that exceed 623 K are related to the proceeding oxidation of the metallic nanoparticles. Their total oxidation occurs at temperatures exceeding 773 K.

3. Conclusion

The influence of oxygen content in an ion beam applied to produce a nanocomposite $(CoFeZr)_x(CaF_2)_{100-x}$ film on its electrical properties has been analyzed.

The application of a combined beam of argon and oxygen causes lowering of the potential barrier on the nanoparticle surfaces. In the course of annealing an additional oxidation occurs — first of the surface and then of the entire metallic nanoparticles.

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