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Hopping Conductance in Nanocomposites $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ Manufactured by Ion-Beam Sputtering of Complex Target in $Ar+O_2$ Ambient Gas

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We report the investigation of a real part of the admittance σ of granular nanocomposites $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ with $0.30 < x < 0.70$ in the dielectric (hopping) regime. An analysis of the $\sigma(T, f, x)$ dependences in the as-deposited and annealed films over the temperature 77 K $< T <$ 300 K and frequency $50 < f < 10^6$ Hz ranges displayed the predominance of an activation (hopping) conductance mechanism with $\mathrm{d}\sigma/\mathrm{d}T > 0$ for the samples below the percolation threshold $x_C \approx 0.76 \pm 0.05$. Based on the earlier models for hopping AC conductance, computer simulation of the frequency coefficient α_f of hopping conductance depending on the probability of jump p, frequency f, and also on the shape of $\sigma(f)$ curve was performed. The experimental and simulation results revealed a good agreement.

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1. Introduction

At present a great interest is shown in the granular composite materials, which consist of Fe- and/or Co-containing soft ferromagnetic nanoparticles embedded in the dielectric matrix, because they are considered as nearly ideal "core" materials for various high-frequency applications. Their low coercivity together with high saturation magnetization, high in-plane anisotropy field, and high resistivity contribute to high power density and low power loss in different applications. Also, such nanocomposites showing much promise as memory media with super-high density of magnetic recording may be used in magnetic recording heads, etc. Besides, most of the electrical, magnetic, and other properties of FeCo-containing nanocomposites vary drastically with the highest sensitivity to the influence of external effects just at x values approaching the percolation threshold x_C [1–7]. This makes the nanocomposites very attractive for the production of sensors, detectors, and similar.

In our previous papers we have studied DC conductivity of the nanocomposite samples of $(Co_{0.45}Fe_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ containing FeCoZr nanoparticles in alumina matrix and deposites either in pure Ar gas [3, 4] or Ar^+–O_2^- gas mixture [5]. It was established that below the percolation threshold x_C DC conductivity is provided by thermally stimulated hopping (tunnelling) of electrons over the dielectric barrier created by the matrix surrounding the metallic nanoparticles [5].

Our papers[5, 6] present the model for DC and AC hopping conductance that takes into account the following hopping conditions:

1. electrons are localized in the potential wells representing the metallic nanoparticles;

2. after a jump of the electron from one neutral well to another, the electrical dipole appears, the electron remains in the second well during the time τ and only then either jumps to the third well (that is determined by the direction of the external electric field) with the probability p or returns to the first well with the probability $1 - p$;

3. interaction of electrons in the potential wells leads to the distribution of the probability density for times τ — $f(\tau_m)$.

In this case the frequency dependence of a real part of the impedance $\sigma(\omega)$ can be written as

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$$\sigma(\omega) = \sigma_{\mathrm{H}} \int \sin \omega t \left[1 - (1-2p) \cos \left(f_{\mathrm{L}}\left(\tau_m\right) \omega \tau\right)\right] \mathrm{d}\tau, \tag{1}$$

where ω — circular frequency of alternating current, σ_{H} — real part of impedance in the high-frequency range, $f_{\mathrm{L}}(\tau_m)$ — distribution of the probability density for the time τ. As follows from the analysis performed in work [4], the Landau distribution in the Moyal approach [8] can be taken in our case for $f_{\mathrm{L}}(\tau_m)$.

As mentioned by Imry [9], in nanomaterials the sign of $\mathrm{d}\sigma/\mathrm{d}T$ on the dielectric side of the metal–insulator transition (MIT) is always positive, whereas on the metallic side it is negative. This change of $\mathrm{d}\sigma/\mathrm{d}T$ sign was used by us in the estimation of the percolation threshold value for the studied nanocomposites $(\mathrm{Co_{0.45}Fe_{0.45}Zr_{0.10}})_x(\mathrm{Al_2O_3})_{1-x}$ at the metallic phase content $0.30 < x < 0.62$.

The aim of the present paper is to investigate some parameters of the developed model for AC hopping conductivity (probability of the jumps p, the time τ associated with staying of the electron in a potential well, radius of the electron localization r_{H}, energies of conductance activation for low $E_{\sigma\mathrm{L}}$ and high $E_{\sigma\mathrm{H}}$ frequencies) using the frequency ω and temperature T dependences of a real part of the impedance in nanocomposite films $(\mathrm{Co_{0.45}Fe_{0.45}Zr_{0.10}})_x(\mathrm{Al_2O_3})_{1-x}$ deposited in $\mathrm{Ar^+}$–$\mathrm{O_2^-}$ gas mixture.

2. Experimental

The $(\mathrm{Co_{0.45}Fe_{0.45}Zr_{0.10}})_x(\mathrm{Al_2O_3})_{1-x}$ films with their thickness ranging from 3 to 6 μm were prepared by ion-beam sputtering of the complex target in a chamber evacuated under the pressure of a mixture of argon $P_{\mathrm{Ar}} = 0.667$ mPa and oxygen $P_{\mathrm{O2}} = 2.4$ mPa. All the technological procedures and experimental techniques are described in [1, 2]. The used method enabled manufacturing of the samples with different metallic phase concentrations ($x = 0.327$, 0.382, 0.426, 0.495, 0.596, and 0.621) under the identical deposition conditions.

The synthesized films were three-phase systems, where the metallic alloy nanoparticles were covered with a complex FeCoZr-oxide "shells" and embedded into $\mathrm{Al_2O_3}$ matrix.

The measurements of AC conductance σ were performed using rectangular samples with silver contacts for the frequencies f between 50 Hz and 1 MHz at the measuring temperatures T_p from 77 K to 300 K for the samples in the initial (as-deposited) state as well as directly after their isochronous (15 min) annealing in a tubular furnace within the temperature range from 398 K to 873 K by 25 K steps. This procedure is described in [10] in more detail.

3. Results and discussion

As follows from the $\sigma(x)$ curves for the measuring temperatures 77 K and 273 K, presented in the normalized form in Fig. 1, over the range $0.30 < x < 0.65$ for the metallic phase content the dielectric-like conductance with $\mathrm{d}\sigma/\mathrm{d}T > 0$ is observed. A linear shape of the $\sigma(x)$ on the semilogarithmic scale $\log(\sigma(x)/\sigma(x = 1.0))$ vs. x for this range of the metallic phase content shows that the $\sigma(x)$ can be approximated by the formula

$$\sigma \sim a \exp\left(+bx\right), \tag{2}$$

where the constant b is strongly dependent on temperature. Let us note that straight lines 1 and 2 in Fig. 1 converge with an increase in x (that indicates reduction of the temperature dependence of σ and its going to the metallic one at $x_{\mathrm{C}} \approx 0.78 \pm 0.05$). This value of the metallic phase content x_{C} can be assumed as the critical (border) concentration when metallic nanoparticles covered with FeCoZr-oxide "shells" touch each other within the alumina matrix, beginning to form a highly conductive net with a very weak temperature dependence of the impedance. This x_{C} value can be considered as an analog of the percolation threshold x_{C} for binary (two-phase) metal–dielectric composites. Let us note that for the $(\mathrm{Co_{0.45}Fe_{0.45}Zr_{0.10}})_x(\mathrm{Al_2O_3})_{1-x}$ films deposited in pure Ar gas the percolation threshold $x_{\mathrm{C}} \approx 0.54 \pm 0.02$ corresponds to an essentially lower value [1]. Such a shift confirms the fact that at sputtering of the target in $\mathrm{Ar^+}$–$\mathrm{O_2^-}$ mixture the as-deposited films possessed excessive (about 5 at.%) oxygen as compared to the stoichiometric alumina matrix [3]. This excess is associated with oxidation of metallic nanoparticles (that was proved in [2] by the Mössbauer spectroscopy) due to the presence of oxygen in the gas mixture at deposition. Taking into account that the diameters of nanoparticles are 6 nm $< D <$ 10 nm [1], a thickness of the FeCoZr-oxide layers around them can be estimated as 0.2–0.3 nm for $x \approx 0.5$.

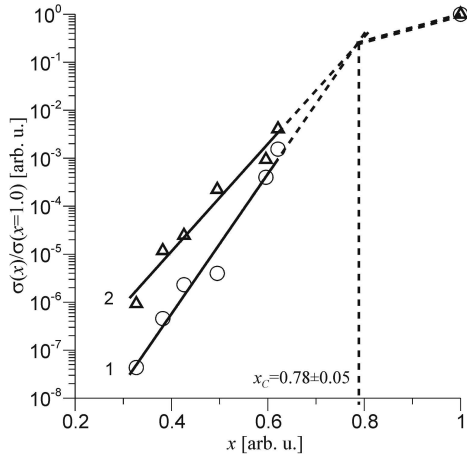

Fig. 1. Normalized real part of the admittance $\sigma_{\mathrm{L}}(x)/\sigma_{\mathrm{L}}(x = 1)$ as a function of the composition in as-deposited nanocomposites $(\mathrm{Co_{0.45}Fe_{0.45}Zr_{0.10}})_{0.495}(\mathrm{Al_2O_3})_{0.505}$ measured at $f = 100$ Hz and at two temperatures T_p: 1 — 77 K, 2 — 273 K.

Figure 2 presents the $\sigma(f)$ dependences of the annealed at $T_{\mathrm{a}} = 548$ K film with $x = 0.495$ between 77 K and

273 K. As can be seen, for low ($f \leq 1$ kHz) and high ($f > 50$ kHz) frequencies $\sigma(f)$ is practically independent of the measuring frequency, showing sigmoid curves at low temperatures.

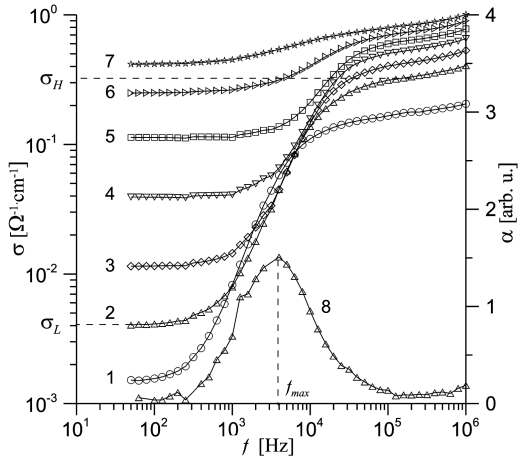

Fig. 2. Frequency dependences of a real part of the admittance σ in the nanocomposite sample $(Co_{0.45}Fe_{0.45}Zr_{0.10})_{0.495}(Al_2O_3)_{0.505}$ after the stepwise 15 min annealing at $T_a = 548$ K for different measuring temperatures T_p: 1 — 77 K, 2 — 128 K, 3 — 158 K, 4 — 188 K, 5 — 218 K, 6 — 248 K, 7 — 273 K and frequency coefficient α for measuring temperature $T_p = 128$ K — 8.

The model for AC hopping conductance developed in our works [5, 6] makes it possible to estimate the values of p and τ_m included into expression (1) using the experimental $\sigma(f)$ curves. As follows from the analysis of Eq. (1) and $\sigma(f)$ dependences (see Fig. 2), the value of p is a quotient of values of real parts of the admittance for low $\sigma_{\rm L}$ and high $\sigma_{\rm H}$ frequencies

$$p = \frac{\sigma_{\rm L}}{\sigma_{\rm H}}\,. \tag{3}$$

To determine τ_m values, it is necessary to extract from the $\sigma(f)$ dependence the frequency coefficient α involved in the relation [11]

$$\sigma(f) \sim f^{\alpha}. \tag{4}$$

Taking a value of $f_{\rm max}$ from $\alpha(f)$ in Fig. 2, we can estimate τ_m using the formula

$$\tau_m \approx \frac{1}{2\pi f_{\rm max}}\,. \tag{5}$$

As follows from Eq. (1), the electron in the time τ with the probability $1 - p$ returns to the well (nanoparticle), from where it has made the first jump. Just these jumps determine a real part of the admittance $\sigma_{\rm H}$ at high frequencies. Since electron overcomes a certain barrier during this jump, the time τ decreases with a temperature growth. This results in the admittance increase so that both τ and $\sigma_{\rm H}$ should be approximately equal to each other. As follows from Fig. 3, the functions $\sigma_{\rm H}(1000/T)$ and $\tau(1000/T)$ may be characterized by the activation energies (0.02 ± 0.005) eV and (0.028 ± 0.005) eV, respectively.

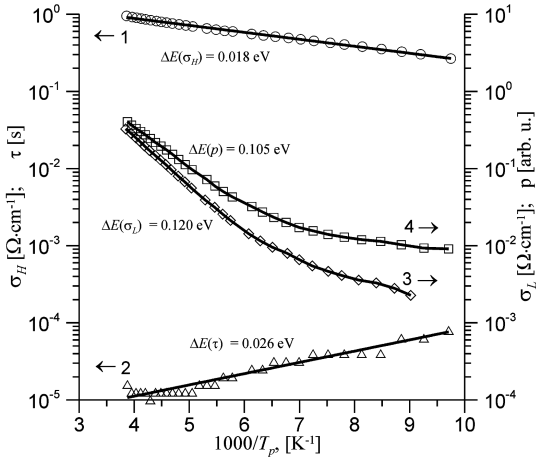

Fig. 3. Temperature dependences of a real part of the high-frequency admittance $\sigma_{\rm H}$ (1), τ (2) for the $x = 0.495$, $f = 1$ MHz and a real part of the low-frequency admittance $\sigma_{\rm L}$ (3) and hopping probability p (4) for $x = 0.495$, $f = 100$ Hz.

As mentioned in Introduction, in accordance with the developed model, the DC conductivity and low-frequency admittance $\sigma_{\rm L}$ are accomplished by hopping of the electron from the second well to the third one with the probability p. This jump is associated with overcoming the additional barrier created by the electric dipole induced due to hopping of the electron from one neutral nanoparticle (well) to another that is neutral, too. In this case the functions $\sigma_{\rm L}(1000/T)$ and $p(1000/T)$ should have much higher activation energies ΔE than $\sigma_{\rm H}(1000/T)$ and $\tau(1000/T)$. This conclusion is confirmed by the curves presented in Fig. 3, where the maximal values of the slopes amount to (0.120 ± 0.05) eV and p (0.105 ± 0.05) eV for $\sigma_{\rm L}$ and p, respectively.

4. Conclusion

It is ascertained in our work that the addition of oxygen O_2^- into Ar^+ ion beam in the process of the $(Co_{0.45}Fe_{0.45}Fe_{0.10})_x(Al_2O_3)_{1-x}$ nanocomposite film deposition shifts the percolation threshold to the values of $x_{\rm C} \approx 0.78 \pm 0.05$, which are higher by 0.24 than those for nanocomposites deposited with a pure Ar^+ beam [1].

The values of the activation energies for high-frequency and low-frequency hopping are estimated as 0.018 eV and 0.125 eV. This marked difference is due to the fact that electrons must overcome an additional barrier when hopping under DC (and low-frequency!) conditions because of the dipole appearance after jump of the electron from one neutral nanoparticle to another.

The experimental functions $\sigma(f)$ and $\alpha(f)$ are in a good agreement with the simulation results.

Acknowledgments

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