Журнал Белорусского государственного университета. Физика. 2023;1:70–77
Journal of the Belarusian State University. Physics. 2023;1:70–77

УДК 538.91, 538.935, 539.232

ПРЫЖКОВЫЙ ТРАНСПОРТ В НАНОГРАНУЛИРОВАННЫХ КОМПОЗИЦИОННЫХ ПЛЕНКАХ ИЗ НАНОЧАСТИЦ СПЛАВА FeCoZr, ОСАЖДЕННЫХ В ДИЭЛЕКТРИЧЕСКИЕ МАТРИЦЫ AL_2O_3 И PZT

А. В. ЛАРЬКИН[1)]***, А. К. ФЕДОТОВ***[2)]

[1)]*Белорусский государственный университет, пр. Независимости, 4, 220030, г. Минск, Беларусь*
[2)]*Институт ядерных проблем БГУ, ул. Бобруйская, 11, 220006, г. Минск, Беларусь*

Представлены результаты изучения характеристик прыжкового переноса электронов в наногранулированных композиционных пленках $(Fe_{0,45}Co_{0,45}Zr_{0,10})_x(Al_2O_3)_{1-x}$ и $(Fe_{0,45}Co_{0,45}Zr_{0,10})_x(PZT)_{1-x}$ с концентрацией металлосодержащих гранул в диапазоне $0,3 < x < 0,8$. Пленки толщиной 2–7 мкм получены методом ионно-лучевого распыления составных мишеней в среде чистого аргона или в смеси $Ar - O_2$, после чего они подвергались ступенчатому отжигу на воздухе в диапазоне температур 398–873 К с шагом 25 К в течение 15 мин. Осаждение композитов в смеси аргон – кислород либо отжиг на воздухе приводили к формированию наночастиц со структурой «ядро – оболочка», где оболочка состояла из собственных оксидов железа и кобальта (FeO, Fe_3O_4, Fe_2O_3, CoO). С точки зрения поведения адмиттанса в зависимости от концентрации, частоты и температуры $\sigma(x, \omega, T)$ в таких нанокомпозитах обнаружены два критических значения концентрации металлических элементов (x) – порог касания (x_{c1}) наночастиц оболочками и порог формирования сплошного проводящего кластера (x_{c2}) из ядер наночастиц (в отличие от понятия «порог перколяции» (x_c) в теории бинарных металлодиэлектрических композитов). Значения x_{c1} показывают концентрацию металлических элементов, при которой наночастицы внутри диэлектрической матрицы начинают соприкасаться друг с другом оболочками и образуют сплошной кластер «ядро – оболочка» с высокой электрической проводимостью между электродами в композитном образце. Поскольку проводимость такого кластера всегда меньше, чем проводимость только металлических наночастиц (как в бинарных нанокомпозитах), то необходимо ввести другую пороговую концентрацию (x_{c2}), при которой металлические ядра наночастиц начинают соприкасаться друг с другом. Определено, что по мере приближения к порогу касания x_{c1} характерное время жизни электронов τ на наночастицах с оболочками полупроводникового типа (FeO, Fe_3O_4) увеличивается с 0,1 до 400,0 мкс. Это приводит к положительному фазовому сдвигу θ между приложенным напряжением и током в пленках, называемому эффектом отрицательной емкости. При этом энергетические характеристики ΔE_1 и ΔE_2, определяемые из температурных зависимостей $\sigma(T)$, снижаются до значений, меньших энергии фонона kT, – от 300 до 1 мэВ. В случае преобладания вокруг наночастиц собственных оксидов железа диэлектрического типа (Fe_2O_3) возрастания τ и снижения ΔE_i не происходит, что приводит к обычному емкостному поведению нанокомпозитов с отрицательным сдвигом фазы θ между током и напряжением.

Ключевые слова: наногранулированные композиты; наночастицы; структура «ядро – оболочка»; прыжковый перенос; эффект отрицательной емкости.

Образец цитирования:
Ларькин АВ, Федотов АК. Прыжковый транспорт в наногранулированных композиционных пленках из наночастиц сплава FeCoZr, осажденных в диэлектрические матрицы Al_2O_3 и PZT. *Журнал Белорусского государственного университета. Физика.* 2023;1:70–77 (на англ.).
https://doi.org/10.33581/2520-2243-2023-1-70-77

For citation:
Larkin AV, Fedotov AK. Hopping transport in nanogranular composite films of FeCoZr alloy nanoparticles deposited into Al_2O_3 and PZT dielectric matrices. *Journal of the Belarusian State University. Physics.* 2023;1:70–77.
https://doi.org/10.33581/2520-2243-2023-1-70-77

Авторы:
Андрей Викторович Ларькин – старший преподаватель кафедры энергофизики физического факультета.
Александр Кириллович Федотов – доктор физико-математических наук, профессор; главный научный сотрудник лаборатории физики перспективных материалов.

Authors:
Andrei V. Larkin, senior lecturer at the department of energy physics, faculty of physics.
larkinav@bsu.by
https://orcid.org/0000-0003-1011-0804
Alexander K. Fedotov, doctor of science (physics and mathematics), full professor; chief researcher at the laboratory of physics of advanced materials.
fedotov@bsu.by
https://orcid.org/0000-0002-7008-847X

HOPPING TRANSPORT IN NANOGRANULAR COMPOSITE FILMS OF FeCoZr ALLOY NANOPARTICLES DEPOSITED INTO AL_2O_3 AND PZT DIELECTRIC MATRICES

***A. V. LARKIN*[a], *A. K. FEDOTOV*[b]**

[a]*Belarusian State University, 4 Niezaliežnasci Avenue, Minsk 220030, Belarus*
[b]*Institute for Nuclear Problems, Belarusian State University, 11 Babrujskaja Street, Minsk 220006, Belarus*

Corresponding author: A. V. Larkin (larkinav@bsu.by)

The paper presents the study of hopping carrier transport parameters (characteristic times and energies) in nanogranular composite films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ with a concentration of metal-containing nanoparticles inside of insulator matrix in the range $0.3 < x < 0.8$. Films of 2–7 μm thick were obtained by ion-beam sputtering of composite targets in pure argon gas or in Ar – O_2 mixture, after which they were subjected to stepwise post-annealing in air in the temperature range of 398–873 K with the 25 K steps for 15 min. Deposition of the films in the argon – oxygen gas mixture or their post-annealing led to the formation of metal-containing nanoparticles with core – shell structure, where the covering shell contained own iron and cobalt oxides (FeO, Fe_3O_4, Fe_2O_3, CoO). It was shown that the behaviour of concentration, frequency and temperature dependences of specific admittance $\sigma(x, \omega, T)$ is controlled by two critical values of nanoparticles' concentrations – touching threshold (x_{c1}) and conducting cluster formation threshold (x_{c2}) (in contrast to a single percolation threshold (x_c) in the theory for binary metal-dielectric composites). The x_{c1} is the concentration when some of nanoparticles inside the dielectric matrix begin to touch each other by shells to form continuous core – shell cluster with high current conductivity between electrodes in the composite sample. Since the conductivity of such a core-shell cluster is always less than the conductivity of only metallic nanoparticles, as in binary composites, we introduce another threshold concentration x_{c2} when the metallic cores of nanoparticles begin to touch each other. We observed that, when composite film approaches the x_{c1} threshold, the characteristic lifetime τ of electrons, extracted from $\sigma(x, \omega, T)$ dependences, on nanoparticles covered with the semiconducting-like shells of native oxides (FeO or Fe_3O_4) increases from 0.1 to 400.0 μs. For this case, we observed a positive phase shift θ between the applied voltage and current in the films, called the negative capacitance effect. At the same time, energy characteristics ΔE_1 and ΔE_2 extracting from $\sigma(T)$ dependences were decreased down to values less than phonon energy kT – from 300 to 1 meV. In the case of the predominance of native oxide of iron with insulating properties (Fe_2O_3) around the nanoparticles, there is no increase in τ and a decrease in ΔE_i. In this case the usual capacitive-like behaviour of nanocomposites with a negative phase shift θ between current and voltage is observed.

Keywords: nanogranular composites; core – shell nanoparticles; hopping transport; negative capacitance effect.

Introduction

Recently, in material science, much attention has been paid to the search for new methods to supply more rapid diagnostics of heterogeneous multifunctional nanomaterials and nanostructures with highly complicated phase structure [1]. The behaviour of physical characteristics in such systems directly depends on their morphology, including phase structure and sizes of homogeneities. Among the wide range of their functional characteristics, which are actively used already in modern engineering, the metal-dielectric nanocomposite materials make it possible, among other things, to use them as wireless elements with inductive-like behaviour. This area of application is based on the so-called negative capacitance effect (NCE) [2], when the delay by phase of electric current from the applied voltage occurs. This effect is observed in some nanostructured materials [3], including metal-dielectric films [4], consisting of a mixture of conductive nanoparticles in non-conductive (insulating) matrixes. This effect is due to the violation of the electrical neutrality of neighboring (closely spaced) highly conductive nanoparticles and the polarisation of the matrix surrounding them as a result of electron tunneling (hopping) between nanoparticles under the action of electric field and electron collisions with phonons, which depends both on temperature and on the intensity of the alternating electric field. As was shown earlier [5], the existence of such a NCE in a wide range of temperatures, including room temperatures, and frequencies depends both on the morphology of metal-dielectric nanostructures (composition, shape and size distribution of conducting and dielectric phases) and on the presence of additional phases arising during synthesis or subsequent heat treatments of these materials.

The paper studies the hopping carrier parameters (characteristic times and energies) transport in alternating current regime in nanogranular composite films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ with the concentrations of the metal-containing FeCoZr alloy $0.3 < x < 0.8$ randomly embedded into dielectric matrix.

Experimental part

The objects of the study were composite nanogranular films 2–7 μm thick deposited by the method of ion-beam sputtering of targets and subjected to stepwise 15 min post-annealings in air in the temperature range of 398–873 K with a step of 25 K [6]. For deposition, we used composite targets, which contained cast metallic $Fe_{0.45}Co_{0.45}Zr_{0.10}$ alloy base with dimensions of 270 × 70 × 14 mm and dielectric strips of Al_2O_3 or PZT of the same size located on its surface at different distances from each other. The distance between the dielectric strips changed monotonically from 3 to 24 mm from one to another sides of metallic base. Such construction of the target made it possible to obtain, in one technological cycle, composite films on the glass-ceramic substrate with a gradient of metal-containing phase (in form of nanoparticles) content x from 0.3 on one side of the substrate to 0.8 on its another side [7]. In case of Al_2O_3 matrix deposition was carried out both in Ar (with pressure $P_{Ar} = 6.0 \cdot 10^{-2}$ Pa) and in Ar – O_2 mixture (with partial pressure $P_{O_2} = 4.3 \cdot 10^{-3}$ Pa) while in case of PZT matrix we used only Ar – O_2 atmosphere (at $P_{O_2} = 2.0 \cdot 10^{-3}$ Pa or $P_{O_2} = 3.0 \cdot 10^{-3}$ Pa).

To analyse the morphology of nanocomposite film, as well as to determine their thickness and chemical composition, a LEO-1455VP scanning microscope (*Carl Zeiss*, Germany) with an attachment for energy dispersive analysis was used. Analysis of the phase composition of the samples before and after annealing was carried out using Mössbauer spectroscopy, electron and X-ray diffraction, and also the X-ray absorption edge methods [8; 9].

To study electric properties of the samples we used an admittance spectroscopy in the temperature range of 77–350 K and alternating current frequencies of 100 Hz – 5 MHz. The admittance was measured by a 4-probe method using a 3532 LCR HiTESTER meter (*Hioki*, Japan). The samples with 10 × 2 mm size were supplied with silver paste electric contacts [10]. The temperature was measured with a thermocouple using an Agilent 34970A multimeter (*Agilent Technologies*, USA). The error of these measurements was no more than 4 %.

Results and discussion

This paper analyses the temperature and frequency dependences of the real part of the specific admittance $\sigma(f, T)$ and phase shift angles $\theta(f, T)$ between current and applied voltage in films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$. The description of $\sigma(f, T)$ curves, including those described in earlier works [10; 11], was carried out on the basis of the improved model of hopping conductivity in a weak electric field (which energy was less than thermal energy of vibrating lattice kT) [12]. This model describes the real part of the admittance by the relation

$$\sigma(f, T) = \sigma_0(f, T) f^{\alpha(f)} \quad (1)$$

with sigmoid-like σ-curves. Here the exponent α, which determines the probability of jumps p between nanoparticles, depends on the frequency as against the known Mott model [13].

Note that in the model being described, an electron jump from one neutral nanoparticle I to another one II can occur in one of two ways: either by tunneling through a barrier or by hopping over the barrier between wells created by a dielectric matrix layer separating nanoparticles of the metallic phase [12]. In both cases, after every jump between wells I and well II, a pair of positively and negatively charged nanoparticles appears creating an electric dipole. The formation of a dipole after the capture of an electron by a nanoparticle influences the dielectric permittivity around dipoles [14] and leads to an increase in the characteristic lifetime τ of an electron on it. This, respectively, results in a delay of the next jump (back on well I or forward on well III) only under the action of a weak electric field, when imparted energy is insufficient for the jump without the help of the additional action of a suitable lattice vibration. Such behaviour of the electron means that it ceases to follow the change in the sign of the alternating electric field, which means that the current is lagging in phase relative to the applied alternating voltage. This delay time can be estimated from the frequency $f_{min} \sim \frac{1}{\tau}$, where f_{min} is the value of frequency above which the electric current lags behind the applied voltage in phase. At the same time, for the frequencies $f > f_{min}$ the phase delay of the next jump from well II back to well I is equal to $2\pi f\tau$, those may become more than 2π, which creates the possibility of a positive phase shift, i. e. NCE.

According to [12], the probability p and the characteristic lifetime τ on $Fe_{0.45}Co_{0.45}Zr_{0.10}$ nanoparticles (as hopping centers) between electron jumps can be estimated from the relations [10; 11]:

$$p = \frac{\sigma_L}{\sigma_H}, \quad (2)$$

$$\tau = \frac{1}{2\pi f_{max}}, \quad (3)$$

where the values σ_L and σ_H in fig. 1, *a*, correspond to the low and high frequency plateaus parallel to the frequency axis on the sigmoid-like $\sigma(f)$ dependence, and f_{max} is the maximum of the corresponding dependence $\alpha(f)$ in the ratio (1). Also the $\sigma(T)$ dependence in equation (1) at a constant frequency in the studied temperature range is described by the model of hopping conduction with the constant energy characteristic ΔE:

$$\sigma(T) = \sigma_0(f) e^{-\frac{\Delta E}{kT}}. \quad (4)$$

The values of ΔE_i are determined from the slope of the straight-line sections of Arrhenius dependences (see the equation (4)) (fig. 1, *b*). An examples of the experimental $\sigma(f, T)$ and $\alpha(f)$ dependences are represented in fig. 1. The $\alpha(f)$ dependences in fig. 1, *b*, were determined by the geometric differentiation of the $\sigma(f)$ curves. These dependences allowed the estimating the σ_L, σ_H, $\alpha(f)$, f_{max} and ΔE parameters introduced in equations (1)–(3).

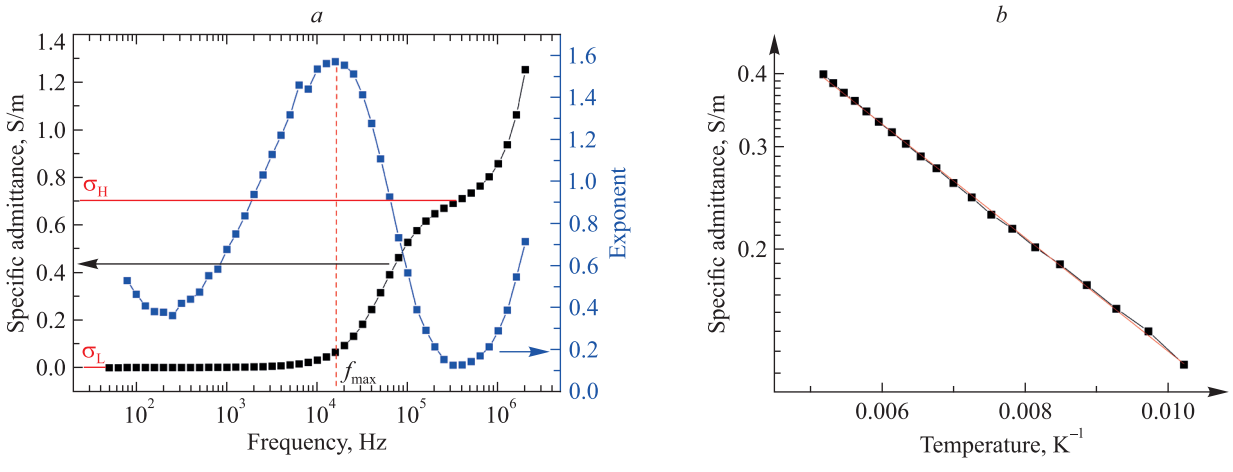

Fig. 1. Examples of the frequency dependence of the real part of the specific admittance $\sigma(f)$ and the exponent $\alpha(f)$ in relation (1) for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.52}(PZT)_{0.48}$ film deposited in Ar – O_2 mixture under $P_{O_2} = 2.0 \cdot 10^{-3}$ Pa and $T = 223$ K (*a*) and Arrhenius curves for $f = 500$ Hz in the region of low T for the film $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.31}(Al_2O_3)_{0.69}$ deposited in an Ar and annealed at $T_{an} = 623$ K (*b*)

Note an important feature of our results – the presence of 2-sigmoid-like character of $\sigma(f)$ dependences (and, correspondingly, the 2-peaks in $\alpha(f)$ dependences according to the model [12]). This was not observed earlier by us, that indicates the impossibility of their study using classical percolation model due to 2-phase (heterogeneous) composition of the samples under consideration.

An analysis of the estimated model parameters of hopping carrier transport in real binary nanogranular composite films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ deposited in pure argon have shown that the characteristic electron lifetime τ on nanoparticles decreases from 12.6 to 1.26 μs with temperature increase in the range 80 K < T < 303 K and for full range of x. In this case, the jump probability for binary structure of nanocomposite always corresponds to the ratio $p \ll 1$ for $x < x_c$, i. e. up to the percolation threshold (dielectric regime of conduction), and $p \to 1$ at $x > x_c$ (metallic regime). The value of the exponent α in relation (1) is close to 0.8 for Mott mechanism of conduction [13] only in composites below the percolation threshold x_c.

Low-temperature annealing at $T_{an} = 623$ K in air of $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ films leads to an increase in the characteristic electron lifetime τ (fig. 2, *a*, inset). Thus for $x = 0.31$ at $T = 303$ K, value of τ increases from 1.26 μs before annealing to 6.17 μs after annealing, which correlates with the formation of iron-based semiconductor oxide shells covering the nanoparticles cores. In addition, annealing leads to the shift of percolation threshold $x_c \approx 0.45$ to higher values of x (to 0.50) for threshold x_{c1} when highly-conductive cluster is formed due to touching of shells around nanoparticle cores. This behaviour corresponds to the activation nature of the admittance, in which the electron hopping probability p increases when phonon energy is higher due to temperature growing (fig. 2, *b*, inset). At the same time, for $x = 0.31$ and $T = 303$ K after annealing at $T_{an} = 623$ K, the value of the exponent α becomes equal to 0.16, which does not correspond to the value $\alpha = 0.8$ for the known Mott mechanism of conduction on alternating current [13].

As follows from the analysis, in $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ nanocomposites deposited in Ar – O_2 mixture, the electron lifetime on nanoparticles increases in comparison with composites deposited in pure Ar. This is due to the formation of semiconducting FeO and Fe_3O_4 oxide shells around metallic cores during deposition,

which also introduces significant changes in the behaviour of $\sigma(x)$ curves. Instead of one critical value (percolation threshold x_c) in Ar deposited metal-dielectric films, the addition of oxygen to the vacuum chamber atmosphere is accompanied by the appearance of two critical values of nanoparticles' concentrations – touching threshold (x_{c1}) and conducting cluster formation threshold (x_{c2}) (in contrast to a single percolation threshold x_c in the theory for binary metal-dielectric composites [15]). The x_{c1} is the concentration when some of nanoparticles inside the dielectric matrix begin to touch each other by shells to form continuous core – shell cluster with high current conductivity between electrodes in the composite sample. Since the conductivity of such a core – shell cluster is always less than the conductivity of only metallic nanoparticles, as in binary composites, we introduce another threshold concentration x_{c2} when the metallic cores of nanoparticles begin to touch each other because the amount of oxygen becomes insufficient to form native oxides (FeO, Fe_3O_4, Fe_2O_3, CoO) which are formed in the shell around the metal cores of the FeCoZr alloy in the sequence FeO → Fe_3O_4 → Fe_2O_3 and should prevent the direct contact between metallic cores.

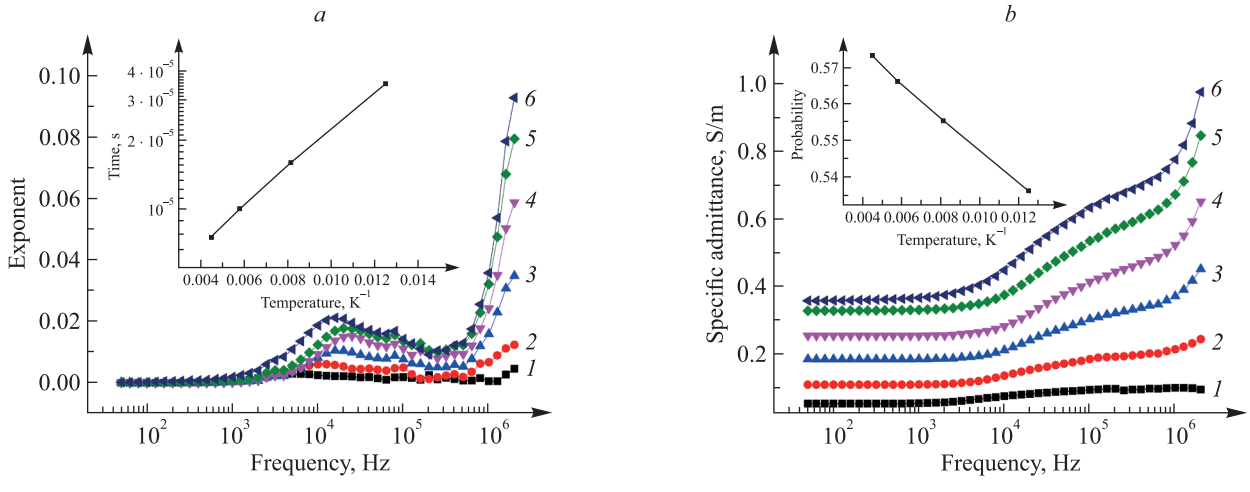

Fig. 2. Frequency dependences of the exponent $\alpha(f)$ in relation (1) (*a*) and the real part of the specific admittance $\sigma(f, T)$ (*b*) for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.31}(Al_2O_3)_{0.69}$ film deposited in an Ar and annealed at $T_{an} = 623$ K for various temperatures: 80 K (*1*), 123 K (*2*), 173 K (*3*), 223 K (*4*), 273 K (*5*), 303 K (*6*). The insets show the temperature dependences of the characteristic lifetime of an electron on nanoparticles (*a*) and the probability of jumping between them (*b*)

The formation of FeO and Fe_3O_4 semiconducting oxides at the initial stages of core formation increases the lifetime (up to $\tau \sim 10^{-4}$ s), which leads to a positive phase shift of current relative to bias voltage applied for concentrations $x < x_{c1}$.

Higher temperature post-annealing in air of $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ films (up to $T_{an} = 873$ K) leads to a further increase in the electron lifetime (fig. 3, *a*) compared to unannealed samples. This is due to additional oxidation of the metal cores with an increase in the proportion of semiconductor oxide phases FeO, Fe_3O_4 in nanoparticles, which further enhances the positive phase shift.

All nanocomposites of the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ type were deposited in Ar – O_2 mixtures. At low partial pressure of oxygen ($P_{O_2} = 2.0 \cdot 10^{-3}$ Pa) the characteristic lifetime of an electron on nanoparticles is about $\tau \sim 10^{-5}$ s, which is insufficient for the existence of the NCE in a wide range of temperatures and frequencies, since for these values of τ the necessary phase delay of the electric current from the applied voltage is not observed. The jump probability in this type of nanocomposites is much lower than in $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ samples, which is associated with a low probability of dipole formation caused by a significantly higher permittivity of the PZT matrix and, as a consequence, an increase in the energy required for this process.

An increase in the oxygen pressure in the deposition atmosphere leads to an increase in τ values. For example, for $x = 0.64$ at $T = 223$ K, the value of τ increased from 6.57 μs (for the sample deposited at $P_{O_2} = 2.0 \cdot 10^{-3}$ Pa) to 79.8 μs (for a sample deposited at $P_{O_2} = 3.0 \cdot 10^{-3}$ Pa). We associate this effect with an increase in the proportion of native iron oxides, including semiconductor FeO and Fe_3O_4, around metal cores, which leads to an increase in the positive phase shift, that is most pronounced in the vicinity of x_{c1}.

Additional annealing in air leads to a slight change in the characteristic electron lifetime (fig. 3, *b*), which does not depend on the partial pressure of oxygen P_{O_2} and only reflects the growth of the amount (and the size)

of iron and cobalt oxide phases around metal cores, including dielectric ones, which is generally not affected the presence of the NCE in $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ nanocomposites, since their morphology is not changed. However, it leads to decrease the temperature range and metal content in which this effect is observed.

Analysis of the energy parameters of carrier transport, estimated on the basis of relation (4), for the case of $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ composites, have shown that, regardless the deposition conditions, the temperature dependences of $\sigma(f, T)$ in Arrhenius scale at each frequency have an activation character with two different energy characteristics corresponding to the slopes of Arrhenius straight lines: ΔE_1 in the range of low temperatures (mostly below 150 K) and ΔE_2 at high temperatures (mostly above 150 K) (fig. 4, *a*).

In this case for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ films deposited in pure Ar, ΔE_2 is always greater than ΔE_1 (for example, for $x = 0.31$ at $f = 1$ MHz, the values are $\Delta E_1 = 20.0$ meV and $\Delta E_2 = 39.5$ meV). The latter probably means that energetically less favourable jumps can be activated only at higher temperatures, where phonons' energies kT are higher. As was shown, for deposited in argon $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ composites, if the energy characteristics ΔE_1 and ΔE_2 lied in the range 15 meV $< \Delta E_i <$ 40 meV, the NCE was not observed at $x < x_c$.

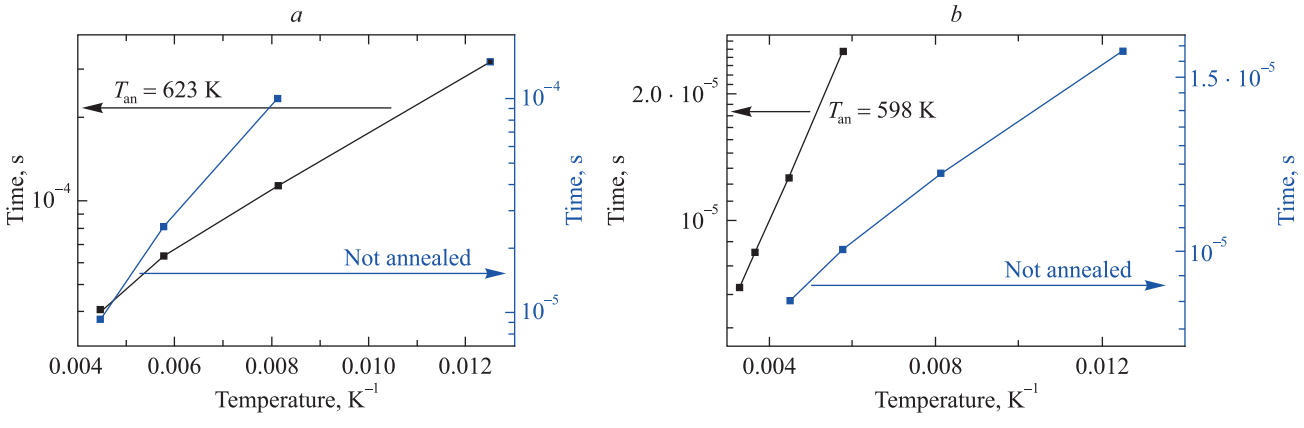

Fig. 3. Temperature dependences of the characteristic electron lifetime τ on nanoparticles before annealing (right ordinate axes) and in the case of annealing in air (left ordinate axes) for $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.38}(Al_2O_3)_{0.62}$ film deposited in Ar – O_2 mixture (T_{an} = 623 K) (*a*) and for $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.52}(PZT)_{0.48}$ film deposited in Ar – O_2 mixture at $P_{O_2} = 2.0 \cdot 10^{-3}$ Pa (T_{an} = 598 K) (*b*)

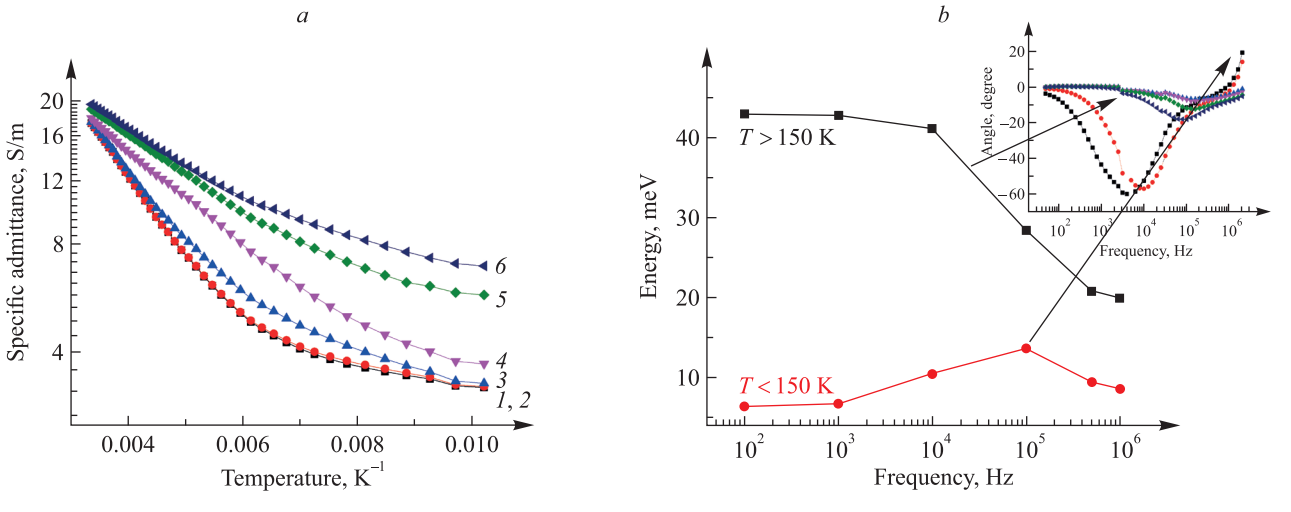

Fig. 4. Temperature dependences of the specific values of the real part of the admittance at different (*1* – 100 Hz, *2* – 1 kHz, *3* – 10 kHz, *4* – 100 kHz, *5* – 500 kHz, *6* – 1 MHz) alternating current frequencies (*a*) and frequency dependences of energy characteristics (*b*) in the region of high and low temperatures. The inset shows the frequency dependences of the phase shift angle in the temperature range of 80–303 K for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.50}(Al_2O_3)_{0.50}$ film deposited in an Ar – O_2 mixture

After annealing in air of this type of samples with $x < x_{c1}$, the energy characteristics slightly decrease compared to unannealed samples (for example, for $x = 0.31$ at $f = 500$ kHz, after annealing the value of ΔE_2 is lowered from 40.6 to 36.5 meV). However, we still do not observe significant contribution to the NCE. We should note that with further increase in oxygen content in the vacuum chamber atmosphere during $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ nanocomposites deposition, which is resulted in the enhancement of the NCE, the energy characteristics are always lowered (fig. 4, *b*).

Here we need to do an important clarification why the NCE is observed in samples with those x, T and f values when formally $\Delta E_i < kT$. In the framework of hopping conductivity model [12] to ensure phase delay of electrons (just resulting in NCE) hopping between potential wells is realised only under subjection of both electric field and phonon energies, i. e. in reality at $\Delta E_i \geq kT$.

As was shown earlier in [16], we observed close behaviour of the energy characteristics of composites $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ extracted from temperature dependences of active R_i and reactive R_{Ci}, R_{Li} elements in their equivalent substitution circuits.

Annealing in air of $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ nanocomposites deposited in an Ar – O_2 mixture at temperatures up to $T_{an} = 873$ K results to the increase the energy characteristics ΔE_i due to the growth of the dielectric oxide Fe_2O_3 contribution to the conductivity of the samples (fig. 5, *a*). However, in those regions of x where the NCE persists, the values of ΔE_i are still smaller than in regions where it is not observed (for example, after annealing at $T_{an} = 623$ K for composite with $x = 0.50$ at $f = 1$ MHz, we have that $\Delta E_1 = 15.0$ meV is less than $\Delta E_2 = 31.4$ meV in the region of low and high temperatures, respectively). It is important to note that after high temperature annealing the region of x, where positive phase shift (with inductive-like behaviour of nanocomposites) expands, so that the energy characteristics ΔE_i decrease over the entire range of x studied.

In $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ nanocomposites deposited in Ar – O_2 mixture at various oxygen partial pressures, the relationship between the phase shift angles θ and the energy characteristics ΔE_i is similar to the previous case (fig. 5, *b*): when the NCE occurs, the energy characteristics are also always less than in the region where it is absent.

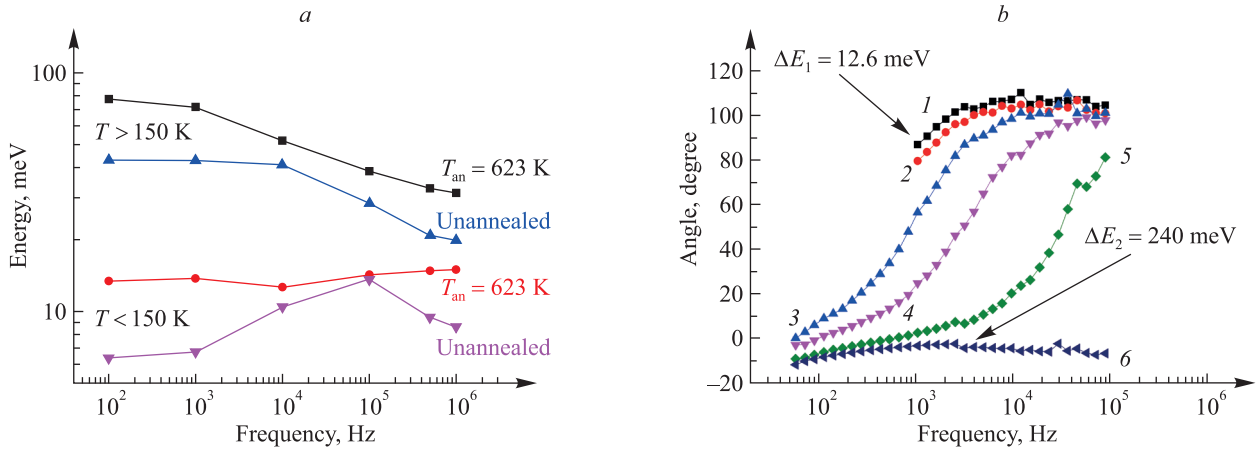

Fig. 5. Frequency dependences of the energy characteristics in the region of high and low temperatures for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.50}(Al_2O_3)_{0.50}$ film deposited in an Ar – O_2 mixture (without annealing and at $T_{an} = 623$ K) (*a*) and the phase angle for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.52}(PZT)_{0.48}$ film deposited in an Ar – O_2 mixture at $P_{O_2} = 3.0 \cdot 10^{-3}$ Pa at different temperatures (*1* – 80 K, *2* – 123 K, *3* – 173 K, *4* – 223 K, *5* – 273 K, *6* – 303 K) with the corresponding energy characteristics (*b*)

Annealing of this type nanocomposites in air up to $T_{an} = 598$ K does not significantly affect the nature of the temperature dependences of the admittance, since their morphology does not change after this heat treatment (for example, in the samples with $x = 0.52$ deposited at $P_{O_2} = 2.0 \cdot 10^{-3}$ Pa, the energy characteristics ΔE_2 at $f = 1$ kHz were 151 meV in the case of annealing at $T_{an} = 598$ K and 154 meV before it).

Conclusions

There were estimated the model parameters of hopping carrier transport (electron lifetime on nanoparticles τ, energy characteristics ΔE_i and hopping probability p, etc.) in nanogranular $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ composite films with different morphology of nanoparticles. It is shown that τ,

ΔE_i and p values significantly depend on the amount, composition and type of native iron oxide phases formed around $Fe_{0.45}Co_{0.45}Zr_{0.10}$ alloy cores in the sequence $FeO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$ regardless of the oxidation method (during deposition or after post-annealing in air). It was found that in the vicinity of the touching threshold x_{c1} the appearance of the negative capacitance effect is observed if the predominance of semiconductor-type iron oxides (FeO, Fe_3O_4) in shells around the nanoparticles cores occurs leading to τ increase (from 0.1 to 400.0 μs) and ΔE_i decrease to values less than kT (from 300 to 1 meV). At the same time, if around cores of nanoparticles dielectric-type native oxide (Fe_2O_3) is prevailed, with the insulating properties close to dielectric matrix, it doesn't cause a sufficient increase in τ and a decrease in ΔE_i leading to the usual capacitive-like behaviour of admittance showing negative phase shift.

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Received 16.07.2022 / revised 08.12.2022 / accepted 08.12.2022.