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ЭКВИВАЛЕНТНЫЕ СХЕМЫ ЗАМЕЩЕНИЯ НАНОГРАНУЛИРОВАННЫХ КОМПОЗИЦИОННЫХ ПЛЕНОК ИЗ НАНОЧАСТИЦ СПЛАВА FeCoZr, ОСАЖДЕННЫХ В ДИЭЛЕКТРИЧЕСКИЕ МАТРИЦЫ Al_2O_3 И PZT

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Представлены результаты изучения характеристик эквивалентных схем замещения наногранулированных композиционных пленок $(Fe_{0,45}Co_{0,45}Zr_{0,10})_x(Al_2O_3)_{1-x}$ и $(Fe_{0,45}Co_{0,45}Zr_{0,10})_x(PZT)_{1-x}$ с концентрацией металлосодержащей фазы в диапазоне $0,3 < x < 0,8$. Пленки толщиной 2–7 мкм получены методом ионно-лучевого распыления составных мишеней в среде чистого аргона и в смеси $Ar – O_2$ с последующим ступенчатым (с шагом 25 К) изохронным (15 мин) отжигом на воздухе в диапазоне температур 398–873 К. Осаждение нанокомпозитов в кислородосодержащей среде либо последующий отжиг на воздухе приводили к формированию наночастиц со структурой «ядро – оболочка», представляющей собой металлические наночастицы $Fe_{0,45}Co_{0,45}Zr_{0,10}$, покрытые оболочками из собственных оксидов железа и кобальта (FeO, Fe_3O_4, Fe_2O_3, CoO). Установлено, что в случае формирования вокруг металлических наночастиц оболочек из включений собственных оксидов железа полупроводникового

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типа (FeO, Fe_3O_4), частотные зависимости полного импеданса нанокомпозитов могут быть описаны на основе эквивалентных схем замещения, содержащих два резонансных RCL-контура, что сопровождается положительным фазовым сдвигом тока относительно приложенного напряжения смещения (так называемым эффектом отрицательной емкости). Если в оболочках вокруг металлических наночастиц увеличивается содержание оксида Fe_2O_3, являющегося диэлектриком, то это приводит к эквивалентным схемам замещения либо с одним резонансным RCL-контуром, либо вообще без RCL-контура, в результате чего эффект отрицательной емкости отсутствует. Показано, что с помощью построения эквивалентных схем замещения нанокомпозитов с разным соотношением металлической (FeCoZr) и диэлектрической (Al_2O_3, PZT) компонент удается описать частотно-температурные зависимости импеданса для элементов схем (R, C, L), соответствующих как отдельным компонентам, так и формирующимся собственным полупроводниковым и диэлектрическим оксидам железа и кобальта в оболочках вокруг металлических ядер.

Ключевые слова: наногранулированные композиты; наночастицы; структура «ядро – оболочка»; эквивалентные схемы замещения; эффект отрицательной емкости.

EQUIVALENT CIRCUITS OF FeCoZr-ALLOY NANOPARTICLES DEPOSITED INTO Al_2O_3 AND PZT DIELECTRIC MATRICES NANOGRANULAR COMPOSITE FILMS

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The paper presents equivalent substitution circuits (ESCs) describing 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 granules 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 or in Ar – O_2 mixture, followed by stepwise (with a step of 25 K) isochronous (15 min) annealing in air in the temperature range of 398–873 K. Deposition of nanocomposites in an oxygen-containing atmosphere or subsequent annealing in air led to the formation of nanoparticles with a core – shell structure consisting of $Fe_{0.45}Co_{0.45}Zr_{0.10}$ metallic alloy cores coated with shells of native iron and cobalt oxides (FeO, Fe_3O_4, Fe_2O_3, CoO). It has been established that when such shells contain semiconductor-type iron oxides (like FeO and Fe_3O_4) the frequency dependences of the total impedance $Z(f, T)$ of nanocomposites can be described using ESCs containing two resonant RCL-circuits, that is accompanied by a positive phase shift of the current relative to the applied bias voltage (the so-called negative capacitance effect). The prevailing of dielectric-like oxides (Fe_2O_3) in shells around metallic cores leads to ESCs either with one resonant RCL-circuit or without it at all. This results in disappearing of the negative capacitance effect when usual capacitive-like behaviour of nanocomposite behaviour is observed. It is shown that if we construct ESCs for nanocomposites with different ratios of the metallic (FeCoZr) and dielectric (Al_2O_3, PZT) components, it is possible to describe the $Z(f, T)$ dependences for every circuit elements (R, C, L) corresponding both to individual phase components in nanocomposites including intrinsic semiconductor- or dielectric-like iron and cobalt oxides in shells around metallic cores.

Keywords: nanogranular composites; core – shell nanoparticles; equivalent substitution circuits; negative capacitance effect.

Introduction

Nanogranular composites are a highly demanded area of modern materials science. Among the wide range of their special properties, the possibility of varying the real and imaginary parts of their admittance in a wide range of values is distinguished, which makes it possible to use them as electrical engineering elements (capacitors, resistors, including wireless pseudo-inductive elements [1]) for a wide range of frequencies and temperatures. The latter area of application is based on the so-called negative capacitance effect, which consists in a positive phase shift between applied voltage and current at a certain phase state of nanogranular composite films. This effect is due to the violation of the electrical neutrality of two neighbouring metallic nanoparticles as a result of tunneling (hopping) of electrons between them (under the influence of both an alternating electric field and temperature). Note that recharging of nanoparticles due to jumps of electrons between them also leads to polarisation of the dielectric matrix surrounding the metal nanoparticles, i. e. the dipoles formation. As was shown in [2], the existence of such an effect in a wide range of temperatures and frequencies depends both on the morphology of composite structures (nanometer-sized conducting and weakly conducting phases, as well as the shape and volume ratio between the latters), and, in particular, on the formation of additional phases (semiconducting and (or) insulating) arising during synthesis and (or) subsequent annealing procedures. This paper is devoted to establishing the relationship between the morphology of 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 and the basic characteristics of equivalent substitution circuits (ESCs), which lead to the effect of negative capacitance in a wide range of frequencies and temperatures.

Experimental part

The objects of the study were nanogranular metal-dielectric composite films deposited by ion-beam sputtering of composite targets and then subjected to isochronous stepwise annealing in air with a step of 25 K for 15 min in the temperature range of 398–873 K [3]. For deposition, composite targets were used, which were a cast metal base 270 × 70 × 14 mm in size prepared from $Fe_{0.45}Co_{0.45}Zr_{0.10}$ alloy with Al_2O_3 or PZT dielectric srips of the same size. These insulating strips were located along metallic plate surface with different distances between them monotonically changing from 3 to 24 mm. This made it possible to obtain composite films on a glass-ceramic substrate in one technological cycle with a gradient of the metal phase x content from 0.3 on one side of the substrate to 0.8 on its other side [4]. In the case of the Al_2O_3 as matrix deposition of the film was carried out either in Ar gas (with $P_{Ar} = 6.0 \cdot 10^{-2}$ Pa) or in Ar – O_2 mixture (at $P_{O_2} = 4.3 \cdot 10^{-3}$ Pa); for PZT matrix we used only Ar – O_2 mixture (at $P_{O_2} = 2.0 \cdot 10^{-3}$ Pa or $P_{O_2} = 3.0 \cdot 10^{-3}$ Pa) as deposition atmosphere.

Scanning and high-resolution transmission electron microscopies with attachments for energy dispersive analysis was used for analysis of the film nanocomposites morphology, as well as determination of their thickness and chemical composition. Analysis of the phase composition of the samples before and after annealing was carried out using the methods of Mössbauer spectroscopy, electron and X-ray diffraction, and also the X-ray absorption edge methods [5; 6].

To study electric properties, we used the method of impedance spectroscopy in the temperature range of 77–350 K and alternating current frequencies of 100 Hz – 5 MHz. The admittance was measured by the 4-probe method using a 3532 LCR HiTESTER (*Hioki*, Japan) meter with an error of no more than 4 %. In the measurements, we used film samples 10 × 2 mm in size, on which electrical contacts were deposited using silver paste [7]. The temperature was measured with a thermocouple using an Agilent 34970A multimeter (*Agilent Technologies*, США).

Results and discussion

This article analyses the amplitude and frequency dependences of the total impedance $Z(f, T)$ of the films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{1-x}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{1-x}$ that allowed us to construct further their ESCs.

As was shown earlier [8–10], the ESCs of composite films under study contain resonant RCL-circuit for certain types of film morphologies. However, these works did not establish a clear relationship between the type of ESC and the morphological features of the films, which determine the manifestation of the negative capacitance effect in the samples. This work is devoted to the solution of this problem.

An analysis of the integral amplitude and frequency characteristics of the $Z(f, T)$ curves have shown that in unannealed $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanocomposites deposited in argon gas, there are two types of $Z(f)$ dependences in samples up to the percolation threshold ($x < x_c$): the decrease in $Z(f)$ with increasing frequency according to the hyperbolic law, which corresponds to the presence of a parallel RC-circuit in the ESC, or $Z(f)$ curves with one maximum, which corresponds to the ESC with one resonant RCL-circuit. Both of these types of ESCs indicate the predominance of the contribution of the dielectric layers of the matrix to the conductivity of the samples. After annealing in air for nanocomposites with small x values, $Z(f)$ dependences exhibit two maxima, which correspond to the presence of two resonant RCL-circuits in ESC. We attribute this effect to the formation of shells with FeO oxides around metallic nanoparticles during annealing.

As can be seen from fig. 1, *a* and *b*, in the case of adding oxygen to the deposition chamber during the synthesis of $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanocomposite films, the $Z(f)$ dependences are characterised by one (at $x > x_{c1}$), which is called by the touching threshold, or two (at $x < x_{c1}$) maxima. Note that the x_{c1} concentration conforms to the x value when the nanoparticles begin to touched each other by oxide shells covering the metallic cores. This such behaviour of the $Z(f)$ curves corresponds to equivalent circuits that include one (fig. 1, *c*) or two (fig. 1, *d*) resonant RCL-circuits. So, in the case of the 2-circuit ESC, the effect of negative capacitance is observed (see the inset to fig. 1, *b*). For the case of the 1-circuit ESC, the character of $Z(f)$ is capacitive-like.

As shown in [5; 11], as a result of annealing in air up to T_{an} = 873 K, additional contributions from FeO and Fe_3O_4 oxide phases of the semiconductor type are formed around the FeCoZr metal cores in the course of the FeO → Fe_3O_4 → Fe_2O_3 transformation chain. In this case (fig. 2, *a*), $Z(f)$ with one resonant maximum before annealing turns into a curve with two resonant maxima after annealing with a corresponding transition of the ESC from the 1-curcuit (see fig. 1, *c*) to the 2-curcuit (see fig. 1, *d*).

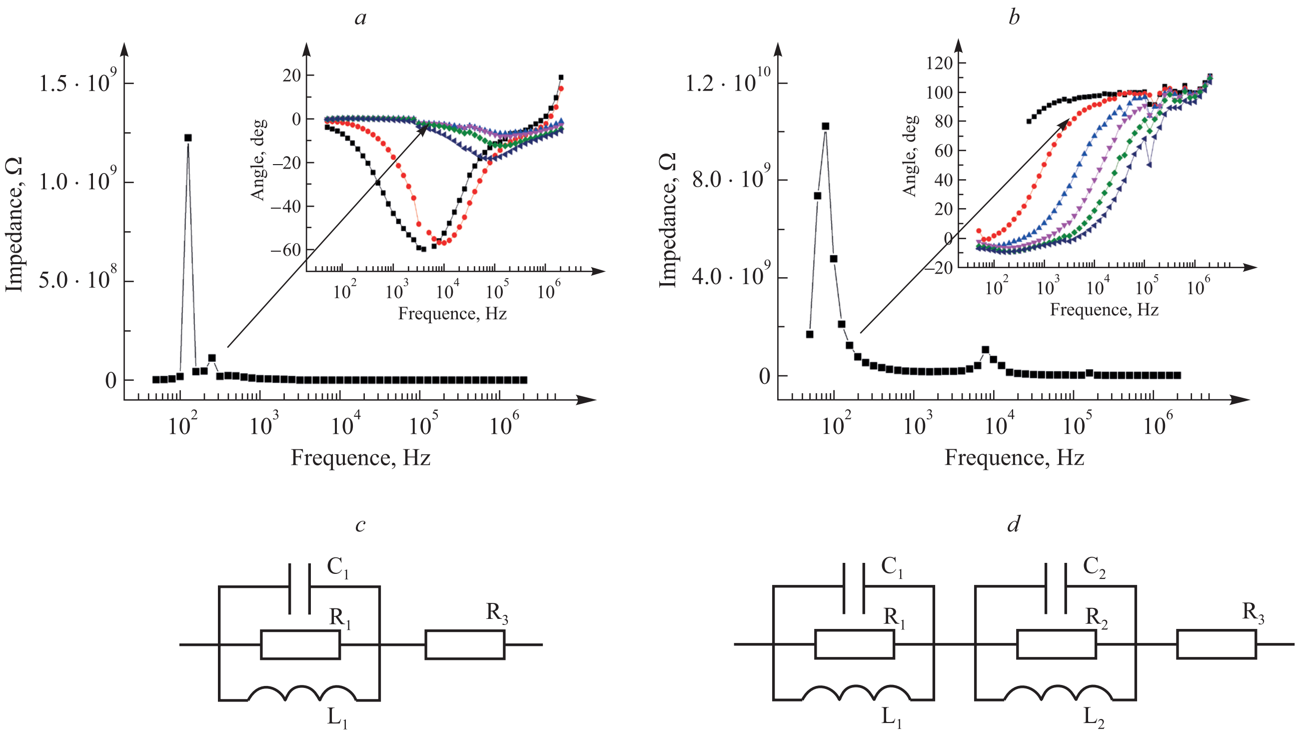

Fig. 1. Amplitude-frequency dependences of the impedance of $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanogranular composite films, deposited in an Ar – O_2 mixture, and the corresponding ESC after (*a*) and before (*b*) the touching threshold:
a – $Z(f)$ dependence with one maximum for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.50}(Al_2O_3)_{0.50}$ film (at T = 223 K);
b – $Z(f)$ dependence with two maxima for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.31}(Al_2O_3)_{0.69}$ film (at T = 123 K);
c – ESC with one resonant RCL-circuit, corresponding to the $Z(f)$ dependence of type (*a*);
d – ESC with two resonant RCL-circuits, corresponding to the $Z(f)$ dependence of type (*b*).
The inset shows the frequency dependences of the phase shift angle $\theta(f)$ in the 80–303 K temperature range

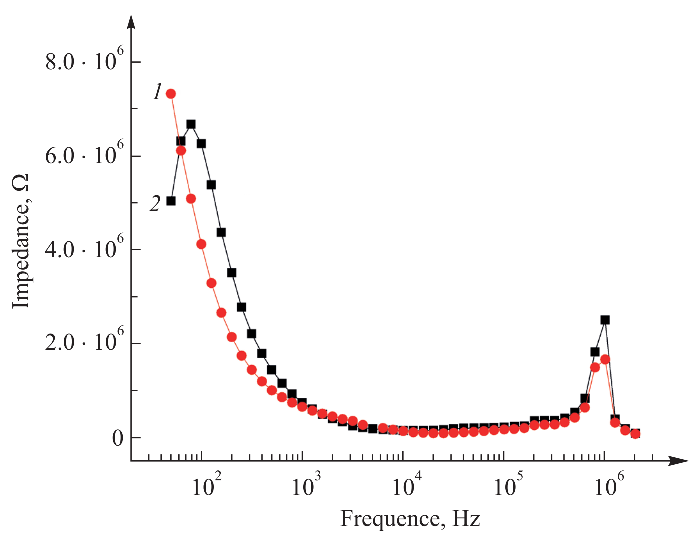

Fig. 2. Transition of the dependence $Z(f)$ with one maximum to $Z(f)$ with two maxima for the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.50}(Al_2O_3)_{0.50}$ film (T = 80 K) after annealing (*1* – unannealed, *2* – T_{an} = 623 K)

Experiments have shown that for nanogranular $(FeCoZr)_x(PZT)_{1-x}$ films, the $Z(f)$ behaviour depends not only on annealing, but also on the partial pressure of oxygen P_{O_2} in the $Ar - O_2$ deposition mixture. An increase in P_{O_2} in the range $2.0 < P_{O_2} < 3.0$ mPa causes a redistribution of oxide phases of the semiconductor (FeO and Fe_3O_4) and dielectric (Fe_2O_3) types around metal cores contributions [12]. This, as it is turned out (fig. 3), changes the $Z(f)$ dependences of the hyperbolic type (before and in the vicinity of the touching threshold x_{c1}) or the dependences with one maximum (beyond the percolation threshold x_{c2} when a continuous conducting cluster is form dur to direct contacting of metallic cores of nanoparticles) to the $Z(f)$ dependences with one or two maxima (before and in the vicinity of x_{c1}) or again to the hyperbolic form beyond the touching threshold x_{c1}).

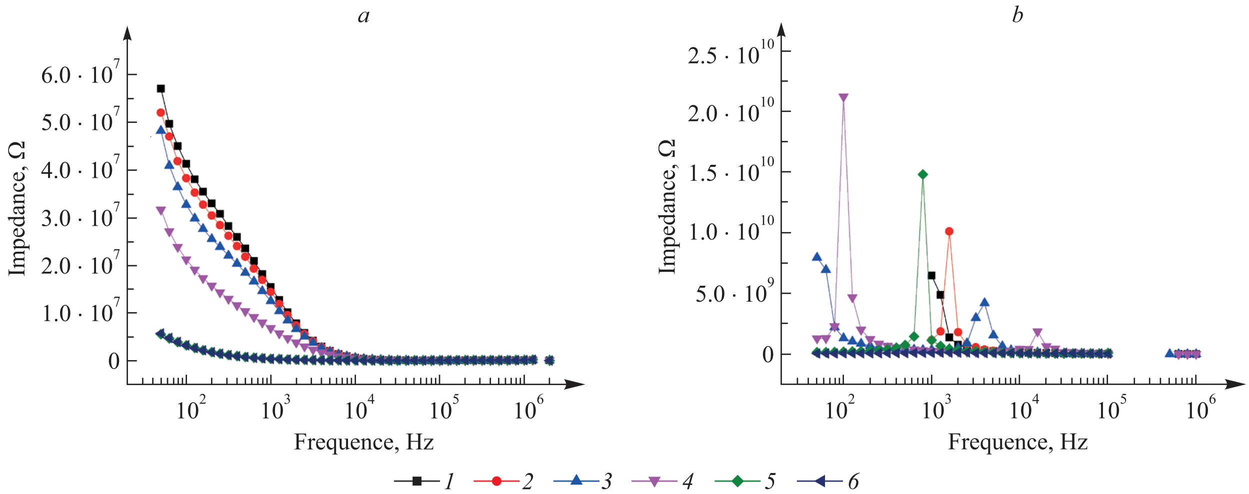

Fig. 3. The influence of the partial pressure of oxygen P_{O_2} in the $Ar - O_2$ deposition mixture on the amplitude-frequency dependences of the impedance of $(FeCoZr)_x(PZT)_{1-x}$ nanogranular composite films at different temperatures (*1* – 80 K, *2* – 123 K, *3* – 173 K, *4* – 223 K, *5* – 273 K, *6* – 303 K) on the example of the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.52}(PZT)_{0.48}$ film:
a – hyperbolic $Z(f)$ dependences at $P_{O_2} = 2.0$ mPa;
b – $Z(f)$ dependences with one or two maxima at $P_{O_2} = 3.0$ mPa

For nanogranular $(FeCoZr)_x(PZT)_{1-x}$ films, as for nanocomposites with an aluminum oxide matrix, we observe the hyperbolic-type curves which correspond to the presence of a parallel RC-circuit in the ESCs, characterised by a joint contribution to the admittance of the PZT matrix interlayers and dielectric native oxide Fe_2O_3. Impedance frequency dependences $Z(f)$ curves with one maximum correspond to equivalent circuits with one resonant RCL-circuit. We attribute them with decrease in the contribution of perforated dielectric intrinsic oxides. Impedance frequency dependences $Z(f)$ curves with two maxima correspond to equivalent circuits with two resonant RCL-circuits, characterised by the contributions to the admittance of both the PZT matrix interlayers and the dielectric intrinsic oxide Fe_2O_3, as well as the semiconducting oxides FeO and Fe_3O_4. Note that in the case when equivalent circuits contain two RCL-circuits, the effect of negative capacitance is also observed, as in the case of composites with an Al_2O_3 matrix.

Additional annealing in air does not lead to a qualitative change in the nature of the amplitude and frequency dependences for $(FeCoZr)_x(PZT)_{1-x}$ films, since the morphology of the samples practically does not change. However, in the region of high x values (fig. 4), the $Z(f)$ dependences with one maximum turn into curves of the hyperbolic type (even for samples deposited at $P_{O_2} = 2.0$ mPa) or 2-step hyperbolic type curves, corresponding to two parallel RC-circuits (contributions of the PZT matrix and Fe_2O_3 phase), can be observed (deposition at $P_{O_2} = 3.0$ mPa). It's caused by the increasing contribution of dielectric oxides to the admittance.

Analysis of contributions of ESC elements to the impedance amplitude and frequency dependences have shown (fig. 5) that in $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanocomposites, deposited in argon gas, if the equivalent circuit includes one resonant RCL-circuit, its active (R_1) and reactive (R_{C1} and R_{L1}) components are characterised by dependences decreasing with increasing temperature with two different activation energies at low (ΔE_1) and high (ΔE_2) temperatures, respectively. In this case, the reactive contributions are always greater than the active ones (for example, $R_1 = 0.889$ GΩ, $R_{C1} = 11.8$ GΩ for $x = 0.31$ at $T = 173$ K), which makes it possible to attribute this circuit element to the Al_2O_3 dielectric matrix. After annealing in air, the nature of the temperature dependences of the ESC elements are not changed, but the value of R_1 decreases (R_1 = 762 MΩ and R_1 = 11.6 MΩ for x = 0.31 at T = 173 K without annealing and in the case of T_{an} = 623 K, respectively), which is associated with an additional contribution to the admittance of the formed semiconducting oxide shells of the FeO type.

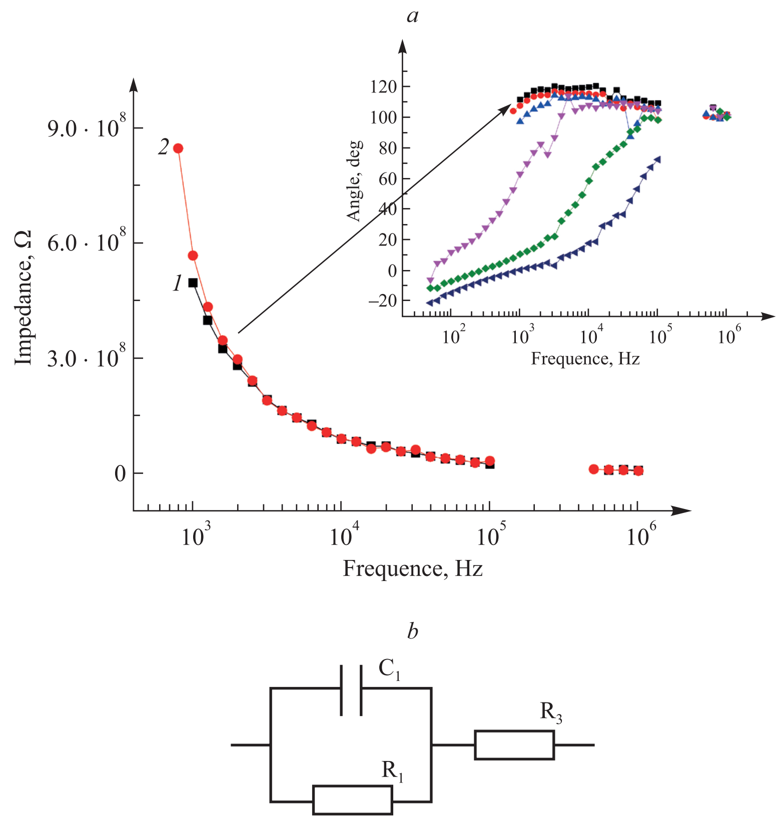

Fig. 4. Hyperbolic $Z(f)$ dependences of impedance of the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.52}(PZT)_{0.48}$ nanogranular composite film (*1* – T = 80 K, *2* – T = 123 K), deposited at P_{O_2} = 3.0 mPa after annealing at T_{an} = 573 K (*a*) and the corresponding EC with one parallel RC-circuit (*b*). The inset shows the frequency dependences of the phase shift angle $\theta(f)$ in the 80–303 K temperature range

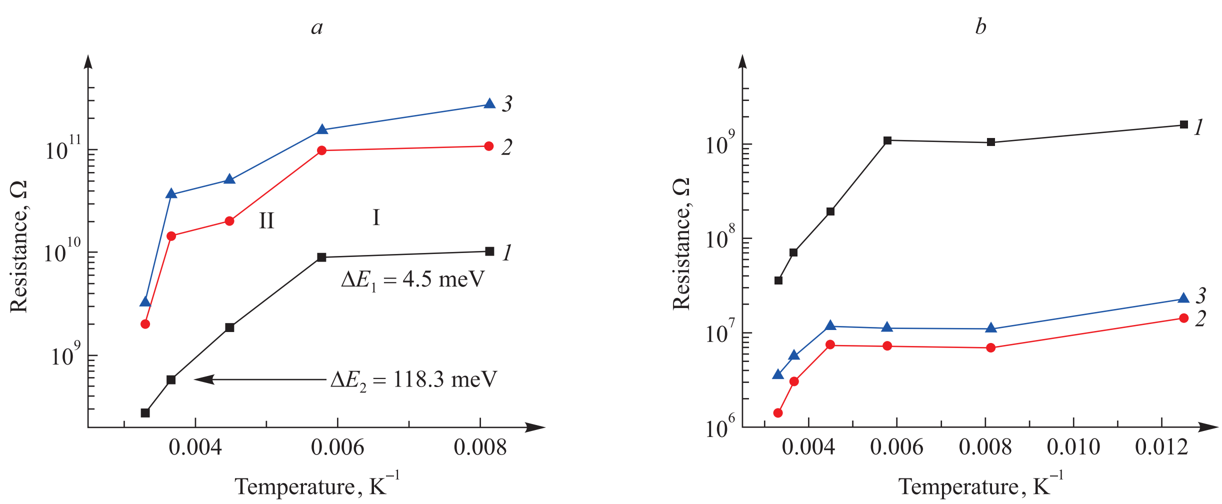

Fig. 5. Temperature dependences of the elements of the 1st (*a*) and 2nd (*b*) resonant RCL-circuits (*1* – R_i, *2* – R_{Ci}, *3* – R_{Li}, i = 1, 2) of the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.31}(Al_2O_3)_{0.69}$ nanogranular composite film, deposited in Ar – O_2 mixture, ESC.
I – low temperature region, II – high temperature region

In $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanocomposites deposited in an Ar – O_2 gas mixture, in the case of the presence of two RCL-circuits in the equivalent circuits, the elements of both of them are characterised by dependences decreasing with increasing temperature (see fig. 5) with two different activation energies ΔE_1 and ΔE_2, respectively, with $\Delta E_2 > \Delta E_1$ (see fig. 5, *a*). The reactive components R_{C1} and R_{L1} of the first RCL-circuit are larger than the active component R_1 (see fig. 5, *a*), which makes it possible to attribute this component with the admittance of the dielectric matrix Al_2O_3 and the dielectric intrinsic oxide Fe_2O_3. The reactive components R_{C2} and R_{L2} of the second RCL-circuit are smaller than the active R_2 circuit (see fig. 5, *b*), which makes it possible to compare this circuit with the contribution of the semiconductor native oxides FeO and Fe_3O_4 to the admittance. If there is only one RCL-circuit in the equivalent circuits, its reactive components R_{C1} and R_{L1} are greater than the active R_1, which makes it possible to compare the circuit with the contribution of the dielectric matrix and dielectric oxide Fe_2O_3 to the impedance.

After annealing these nanocomposites in air up to T_{an} = 623 K, the active resistances of the equivalent circuit (R_1, R_2, R_3) increase in comparison with unannealed samples (fig. 6, *a* and *b*), which, naturally, can be associated with the formation of additional oxide phases of Fe and Co around nanoparticles. The reactances (R_{C1}, R_{L1}, R_{C2}, R_{L2}) synchronously demonstrate different behaviour with respect to annealing (fig. 6, *c* and *d*) depending on the temperature range of measurements (they increase in the low temperature region and decrease in the high temperature region compared to nanocomposites not subjected to annealing procedure). The latter makes it possible to ascribe this to the redistribution of the contributions from various Fe oxide phases formed during annealing.

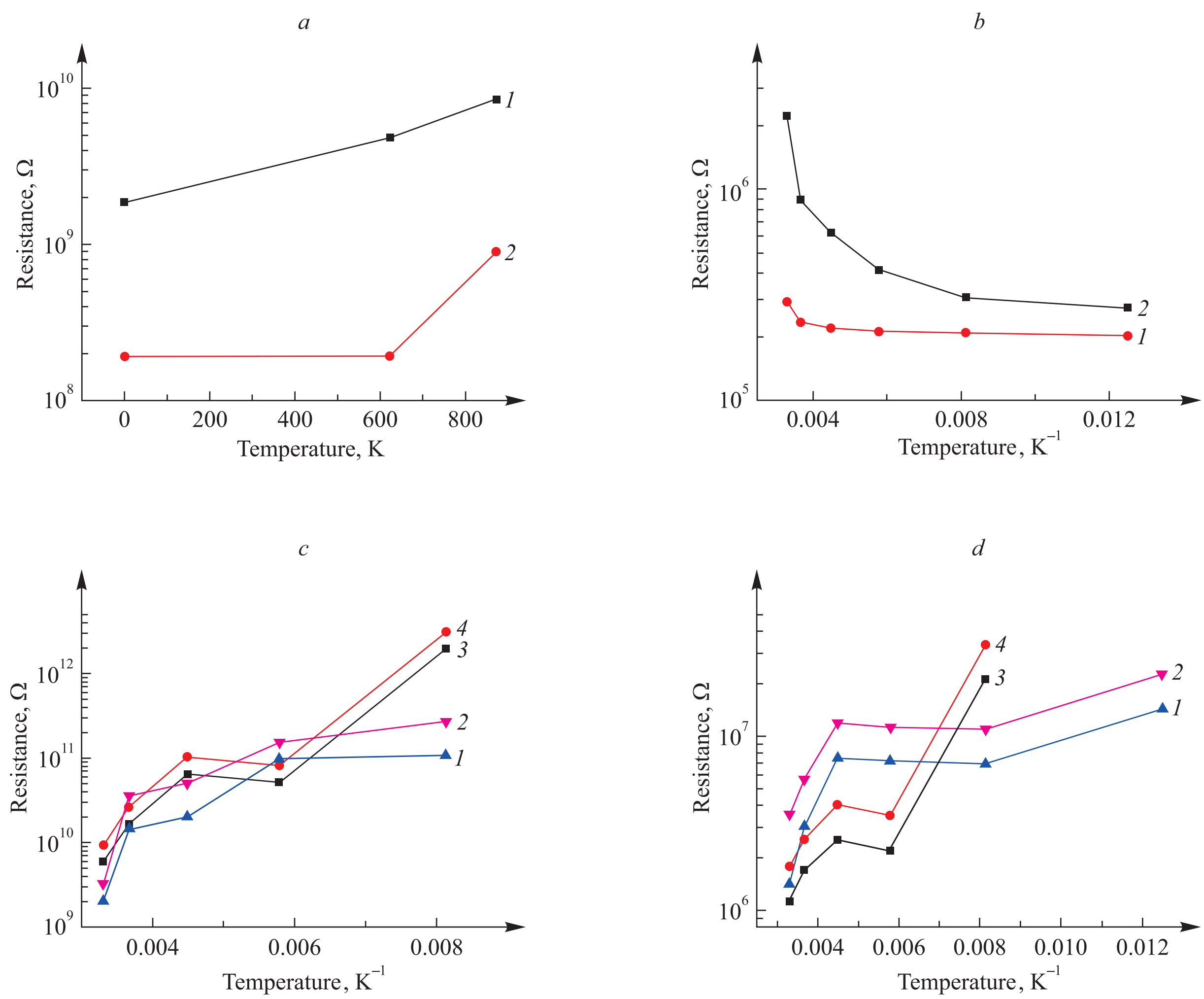

Fig. 6. Dependences of the resonant RCL-circuits active resistances (*1* – R_1, *2* – R_2) on the annealing temperature (*a*) and the temperature dependences (*1* – unannealed, *2* – T_{an} = 623 K) of the additional resistance R_3 (*b*), as well as the reactive elements (*1* – R_{C1}, unannealed; *2* – R_{L1}, unannealed; *3* – R_{C1}, T_{an} = 623 K; *4* – R_{L1}, T_{an} = 623 K) of the first (*c*) and the second (*1* – R_{C2}, unannealed; *2* – R_{L2}, unannealed; *3* – R_{C2}, T_{an} = 623 K; *4* – R_{L2}, T_{an} = 623 K) (*d*) resonant RCL-circuits of ESC in the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.31}(Al_2O_3)_{0.69}$ nanogranular composite film, deposited in Ar – O_2 mixture

An increase in the annealing temperature up to T_{an} = 873 K leads to an additional increase in active resistances (see fig. 6, *a*), which can be associated with the formation of the Fe_2O_3 dielectric oxide phase. In this situation, in the case of the appearance of the negative capacitance effect, the largest increase is noticeable in the active component R_2 of the second RCL-circuit, which is most likely due to the contribution of semiconducting phases (especially narrow-gap Fe_3O_4) that appear during the above-mentioned chain of $FeO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$ transformations.

In $(FeCoZr)_x(PZT)_{1-x}$ nanocomposites deposited in Ar – O_2 mixture at a partial oxygen pressure of P_{O_2} = 2.0 mPa, in the case of the presence of one RC-circuit in the ESC, its elements are characterised by decreasing dependences with two different activation energies at low and high temperatures, respectively (as in the case of ESC with one RCL-circuit for samples with an Al_2O_3 matrix, when the contributions of the dielectric alumina matrix and Fe_2O_3 oxide predominate, as well as a negative phase shift).

With an increase in P_{O_2} in the deposition atmosphere to 3.0 mPa, in the case of the presence of two RCL-circuits in the ESC, their elements are also characterised by $R_i(T)$ dependences decreasing with increasing temperature with two different activation energies in the region of low and high temperatures, respectively (as in the case of equivalent circuits for samples with an Al_2O_3 matrix, when the effect of negative capacitance is observed due to the predominance of the contributions of semiconductor oxides FeO and Fe_3O_4).

After annealing in air up to T_{an} = 598 K, the $(FeCoZr)_x(PZT)_{1-x}$ samples show an increase in the values of the active and redistribution of the reactive components of the equivalent circuits, associated with the formation of additional oxide phases.

Based on the selected temperature dependences of active R_i and reactive R_{Ci}, R_{Li} ESC elements for unannealed nanogranular film composites $(FeCoZr)_x(Al_2O_3)_{1-x}$ and $(FeCoZr)_x(PZT)_{1-x}$ (in the case of the presence of two RCL-circuits in ESC), we have used the improved model of hopping conduction [12] in a weak electric field ($E < kT$), to extract the average characteristic hopping activation energies ΔE_i, affecting various elements of the equivalent circuit. The procedure for such an assessment takes into account the fact that the value of ΔE_i characterises the potential energy of a pair of charges (which, according to [13], form a dipole) located in adjacent potential wells. Then, based on the relation

$$r = \frac{e^2}{4\pi\varepsilon_0\varepsilon\Delta E},$$

it is possible to estimate the average hopping lengths r_i (for these estimations we used the permittivity of the matrix substance as ε = 10 and ε = 34 for Al_2O_3 and PZT, respectively).

Estimates made for $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanocomposites, deposited in Ar – O_2 mixture at x = 0.31 (up to the touching threshold), gave the following results. The average characteristic hopping activation energies ΔE_i turned out to be such that the barrier is permeable in the case of hopping through phases corresponding to both RCL-circuits (ΔE_1 = 3.5 meV in the high temperature region and ΔE_2 = 7.3 meV in the low temperature region). At the same time, the corresponding average electron hopping length r_i for the elements of the second RCL-circuit, the presence of which accompanies the appearance of the negative capacitance effect, is always less (r_1 = 162.9 nm in the high temperature region and r_2 = 78.5 nm in the low temperature region). The estimates made indicate that in $(FeCoZr)_x(Al_2O_3)_{1-x}$ nanocomposites, tunneling (jumping) in the low temperature region occurs between metallic cores through the nearest native oxide shells surrounding them and the thinnest interlayers of the Al_2O_3 dielectric matrix (fig. 7, *a*).

For $(FeCoZr)_x(PZT)_{1-x}$ nanocomposites deposited in Ar – O_2 mixture at a partial oxygen pressure of P_{O_2} = 3.0 mPa, at x = 0.52 (in the vicinity of the touching threshold), the average electron hopping length r_i calculated according to (1) has a value of ~4 nm (r_2 = 4.33 nm and r_2 = 3.58 nm when calculated relative to R_2 and R_{C2}, R_{L2} respectively in the low temperature region). This estimation indicates that, at low temperatures, tunneling (jumping) is most likely carried out between metallic cores through the nearest surrounding shells of native semiconducting oxides (fig. 7, *b*).

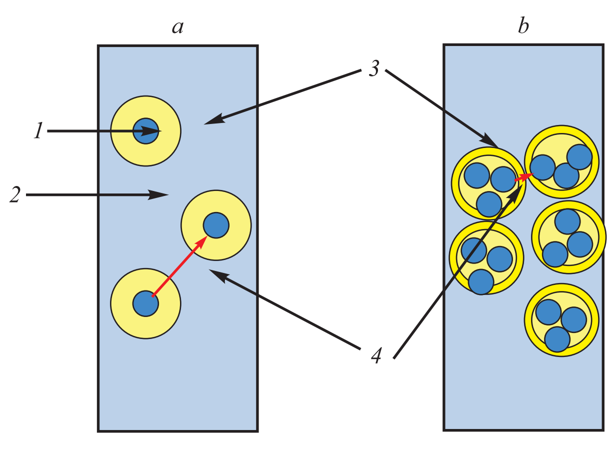

Fig. 7. Schematic representation of the morphology of the $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.31}(Al_2O_3)_{0.69}$ nanogranular composite films, deposited in Ar – O_2 mixture (*a*) and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_{0.52}(PZT)_{0.48}$ films, deposited in Ar – O_2 mixture at P_{O_2} = 3.0 mPa (*b*):
1 – metal cores from FeCoZr alloy;
2 – Al_2O_3 or PZT dielectric matrix;
3 – various oxide phases formed during the chain of transformations $FeO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$ around metal cores;
4 – direction of electron tunneling (jumping) (red arrows)

Conclusion

The finding of nanogranular $(FeCoZr)_x(Al_2O_3)_{1-x}$ and $(FeCoZr)_x(PZT)_{1-x}$ composite films equivalent circuits in the region of different relative concentrations of metallic (FeCoZr) and dielectric (Al_2O_3, PZT) phases has been carried out. The found ESCs made it possible to relate the types of frequency and temperature dependences of the impedance for the circuit elements corresponding both to the initial components (metal, dielectric) and those formed in the sequence FeO $\rightarrow$ Fe_3O_4 $\rightarrow$ Fe_2O_3 around the metallic cores from the FeCoZr alloy their native oxides of iron (either semiconducting or dielectric). It has been found that if inclusions of intrinsic semiconductor-type iron oxides (FeO, Fe_3O_4) dominate in the shells around the metallic cores, the equivalent circuits of the nanocomposites studied contain two resonant RCL-circuits. In this case, the samples exhibit a positive phase shift of the current relative to the bias voltage (the negative capacitance effect). The predominance of dielectric-like native oxide of iron (Fe_2O_3) in the shells around the metal cores leads to equivalent circuits either with one resonant RCL-circuit or without it, so that in this case the negative capacitance effect is absent. It is shown that the separation of the temperature dependences of active and reactive elements in equivalent circuits makes it possible to estimate the hopping characteristics (average energies and lengths), which, taking into account the phase composition of nanoparticles, makes it possible to establish between which phases tunneling (hopping) took place.

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