Influence of Matrix Type on Negative Capacitance Effect in Nanogranular Composite Films FeCoZr-Insulator

T. N. Kołtunowicz[1], P. Zhukowski[1], A. K. Fedotov[2], A. V. Larkin[2],
A. Patryn[3], B. Andryevskyy[3], A. Saad[4], J. A. Fedotova[5], V. V. Fedotova[6]
[1]*Lublin University of Technology,*
Nadbystrzycka St. 38d, 20-618 Lublin, Poland
[2]*Belarusian State University,*
Nezavisimosti Av. 4, 220030, Minsk, Belarus
[3]*Koszalin University of Technology,*
Śniadeckich St. 2, 75-453 Koszalin, Poland
[4]*Al-Balqa Applied University,*
P.O. Box 2041, 11953 Amman, Salt, Jordan
[5]*National Center for Particles and High Energy Physics,*
Bogdanovich St. 153, 220040 Minsk, Belarus
[6]*Scientific-Practical Materials Research Center of NAS of Belarus,*
P. Brovka St. 19, 220072 Minsk, Belarus
t.koltunowicz@pollub.pl

***Abstract*—We observed an inductive contribution to impedance in granular $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{(1-x)}$ and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{(1-x)}$ nanocomposite films deposited in $Ar + O_2$ atmosphere. The films with $x \approx 0.30$ (in dielectric regime) demonstrated negative capacitance effect which were explained by hopping conductance of electrons over FeCoZr nanoparticles covered with complicated CoFe-oxides and embedded into dielectric matrix. In particular, at the determined conditions such a structure of nanocomposite resulted in the increase of hopping electron mean life time on nanoparticles and delay its returning jump under subjection of alternating electric field that created the possibility for positive angles of the phase shifts θ and properly negative capacitance (inductive-like contribution) effect.**

***Index Terms*—Metal-insulator composite, nanocomposites, negative capacitance effect, equivalent circuits.**

I. INTRODUCTION

Investigation of the granular nanocomposites containing dielectric matrix with nanoparticles (NPs) of soft FeCo-based alloys are of a great interest for the material science. The interest to such systems is mainly due to the possibilities for their application for engineering of shields protecting against the HF electromagnetic radiation, in highly-Ohmic resistors and for other purposes [1]. The fact that some nanocomposites being on dielectric side of insulator-metal transition (IMT) possess the semiconducting properties, but their manufacturing is usually cheaper, determines also their possible usage as active and reactive elements in electrical circuits [2]. As was noted in [3], some of the metal-dielectric nanocomposites can be recommended as miniature planar coilless inductive elements in electrotechnical circuits. The last recommendation was connected with the observed effect of negative capacitance (NC) effect firstly observed in our paper [4] at the investigation of impedance in granular nanocomposite films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{(1-x)}$ deposited in $Ar + O_2$ atmosphere.

Capacitance spectroscopy of disordered materials and devices exhibits the phenomenon of NC that corresponds to an inductive contribution to impedance. Although the physical origin of NC has been discussed in the literature (see, [5]–[9]), the concept of its explanation is still not widely recognized. Interpretations of the NC phenomenon in [5]–[7] were based on considerations of purely electrostatic charge redistribution inside the device and explained by reference to impact ionization, injection of minority carriers or an imaginary component in the carrier mobility. Some theories proposed were based on Drude model [6] as well as space charge limited conduction [3] to explain NC effect in disordered solids by scattering trap states by energies.

In our works [4], [10]–[12] we observed NC effect in metal-dielectric nanocomposite films FeCoZr-Alumina. It was very weak in the samples deposited in pure Ar gas atmosphere but strongly enhanced after incorporation of oxygen into vacuum chamber and additional annealing procedure [12]. The main goal of this paper is to compare

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the NC effect in as-deposited (unannealed) nanocomposite samples with $x \approx 0.30$ being on dielectric side IMT which contain oxidized CoFeZr nanoparticles embedded into dielectric matrixes – either Al_2O_3 or PZT.

II. EXPERIMENTAL

Granular $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{(1-x)}$ (set 1) and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{(1-x)}$ (set 2) nanocomposite films were prepared using ion-beam sputtering of compound target in vacuum chamber filled with $(Ar + O_2)$ gas mixture with partial pressures $P_{O2} = 0{,}6 \div 5{,}0)$ mPa [13]. The used deposition method (see details in [3], [13]–[15]) allowed to obtain in one technological cycle the whole set of samples with different metallic phase concentrations in the range of 30 at.% < x < 65 at.%. In this method the compound target to be sputtered consisted of alloy $Co_{0.45}Fe_{0.45}Zr_{0.10}$ plate with dimensions of 280 × 80 mm^2 with dielectric stripes (either alumina or PZT) of 8 mm width arranged on its surface. Irregular distribution of alumina stripes (with continuously increased space between them) at the target surface allowed getting a wide value of metal-to-dielectric ratios x (depending on the mutual arrangement of the target and substrates) in one technological cycle. Owing to the specific design of the vacuum set-up, sputtering of the target was carried out at low enough pressure that assured purity of the deposited films and extremely low content of Ar in them.

The studied samples (films) were sputtered at the temperature ≈ 373 K onto glass-ceramic substrates for electric measurements and thin aluminum foils for Mossbauer investigations. Thicknesses of the composite films were 1 to 6 μm and dimensions of the substrate with the deposited films was 250 mm long, 50 mm wide and 0.6 mm thick. Measurements of the structure and chemical elements content (with accuracy of ~ 1%) of the composites were made using Scanning Electron Microscope (SEM) LEO 1455VP with a special micro-probe X-Ray analyzer. Thicknesses of the films was measured on SEM with accuracy ~ 2-3% on cleavages of the samples studied.

The as-deposited films were cut to give rectangular samples with dimensions 10 mm length and 2 mm width, on which electrical probes were prepared using a special silver paste. Measurements of admittance $G(f, T)$ of the samples studied have been performed at the measuring temperatures T from 80 K to 373 K. Set-ups for the $G(f, T)$ measurements used either precision AC bridge HIOKI 3532 LCR HiTESTER (for the frequency range of 50 Hz - 100 kHz) or precision Hewlett Packard LCR-meter HP 4284A (for measurements at the frequencies 100 kHz - 1 MHz) and a special PC-based control systems.

III. RESULTS AND DISCUSSION

During the study of full impedance $Z(f, T)$ in as-deposited nanocomposites we have found the presence of NC effect (inductive-like contribution to impedance) in the samples of both types (sets 1 and 2). This effect consisted in positive phase angle shift $\theta(f)$ observed in some frequency and temperature ranges. The observed unusual behaviour of $Z(f, T)$ dependencies is analyzed by us in terms of equivalent circuits which can describe the frequency/temperature impedance behaviour of the studied nanocomposites. To create the equivalent circuits, we firstly analyze the frequency dependences of full impedance $Z(f)$ presented in Fig. 1 at temperatures where NC effect was observed.

As is seen from the curves in Fig. 1, the full impedance frequency dependences $Z(f)$ of the studied samples reveals the presence of either one maximum (in set 1 sample) or two maxima (in set 2 sample) when measuring at different temperatures. As is seen from inset in Fig. 1b, the $\theta(f)$ curve for the set 2 sample crosses $\theta = 0$ value at the frequency f close to the position of the left maximum. The detailed analysis of $Z(f)$ and $\theta(f)$ curves (and also fitting of frequency/temperature dependencies of real and imaginary parts of impedance) for the set 1 and 2 samples of the same composition allowed us to propose that their behaviour can be described by equivalent circuit included two series connected *RLC* resonance circuits that imaged in Fig. 2.

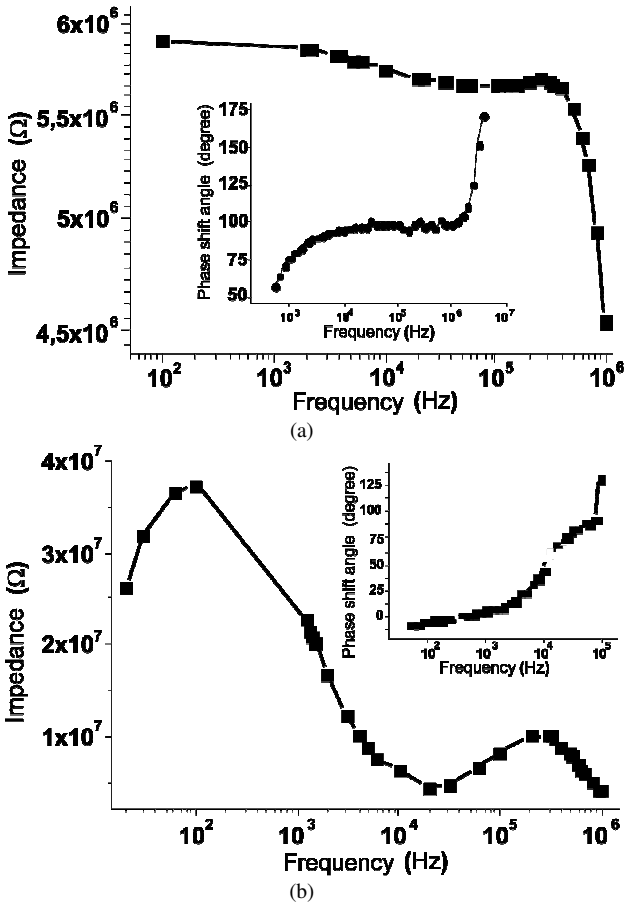

Fig. 1. Frequency dependencies of full impedance $Z(f)$ in the as-deposited samples with $x \approx 0.30$ for set 1 measured at $T = 120$ K (*a*) and set 2 measured at $T = 303$ K (*b*). Insets present the frequency dependencies of phase shift angles $\theta(f)$ for the same samples.

Such behaviour of the studied nanocomposite samples supports the fact that every of two resonance *RLC*-circuits describing $Z(f)$ have their own resonance frequency

$$f_i = \frac{1}{2\pi\sqrt{L_i C_i}}, \qquad (1)$$

where $i = 1, 2$. It differs fundamentally from equivalent circuit of nanocomposites, which were deposited at the lack of oxygen in vacuum chamber [10], [11].

Comparison of θ(*f*) curves in insets in Figs. 1a and 1b shows that the first maximum for the set 1 sample should be presented for $f \leq 100$ Hz. Note also that as follows from θ(*f*) curve in insert in Fig. 1b, the frequency at which phase angle shift $\theta = 0°$ should coincide with the position of the first maximum on frequency scale (self-resonant frequency f_1 in formula (1)).

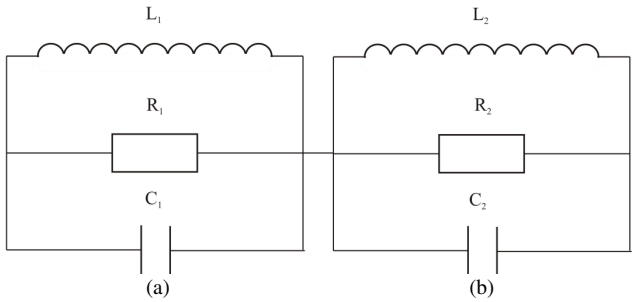

Fig. 2. Equivalent circuits of the set 1 and 2 samples.

As was shown in [12], in the as-deposited set 1 samples NC effect (inductive-like behaviour) accorded to positive θ(*f*) values was observed only at temperatures lower than 150 K but after special heat treatments it was also observed at $T > 250$ K. At the same time, as is seen from Fig. 1b, $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{(1-x)}$ nanocomposite sample (set 2) displays large positive values of the phase angle shift θ, approaching +90°, at $f > 10^4$ Hz at room temperature even in the as-deposited state.

The observed in [4], [10], [11] inductive-like contribution into temperature dependence of impedance for $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{(1-x)}$ (set 1) films deposited in $Ar + O_2$ atmosphere was attributed to inhomogeneous distribution of current-conducting routes with self-crossing parts. This resulted in the formation of coil-like current-conducting routes in the samples studied giving inductive-like contribution to impedance.

As was shown earlier in [4], [10], [11] for nanocomposites $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{(1-x)}$, two maxima in *Z*(*f*) were observed only for the films deposited in mixture of $Ar + O_2$ when metallic NPs were covered with FeCo-based oxide "shells". So we can suppose that one of two resonance *LCR* circuits in Fig. 2 belongs to dielectric matrix while another one to FeCo-based oxide "shells".

The observed *Z*(*f, T*) and θ(*f, T*) dependences for the composites studied can be explained on the base of the AC/DC hopping model developed in our previous works [3], [12], [16]–[18]. This model takes into account that electrons are localized in the potential wells (the metallic NPs embedded into amorphous dielectric matrix), and after a jump of the electron (for times of the order of 10^{-13} s) from one neutral well to another, the electrical dipole appears. The interaction of electrons, trapped by the neighbourhood metallic nanoparticles (potential wells) and surrounded by polarized dielectric matrix, leads to the redistribution of the probability density *p* for the next jump (forward or backward) for some time

$$f \leq \frac{1}{2\tau_m} \approx f_{\min}. \qquad (2)$$

In this case the frequency dependence of a real part of impedance can be written as the known Mott relation [19]

$$Z'(f) \sim f^{-\alpha}, \qquad (3)$$

where *Z*′ – real part of impedance and the exponent α is the so-called frequency factor. As is seen in Figs. 3, *Z*′(*f*) dependencies really follows the Mott law (3) in the frequency range $f >$ (1-10) kHz and at $T < 150$ K for the set 1 sample and even at room temperature for set 2 sample.

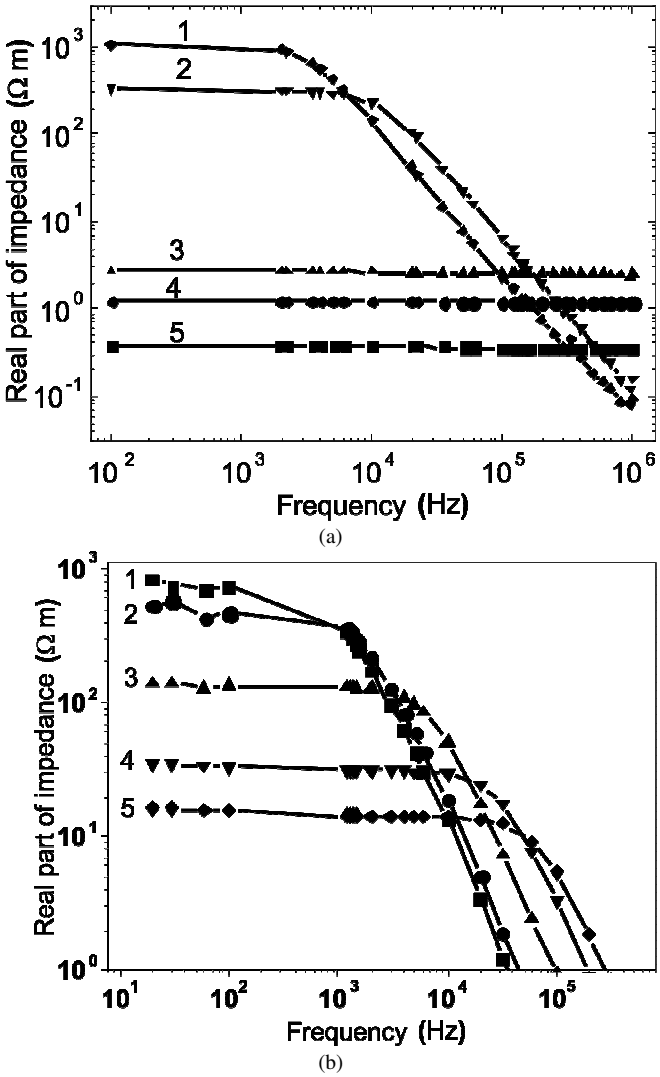

Fig. 3. Frequency dependences of the impedance real part for the set 1 (*a*) and set 2 (*b*) samples with $x \approx 0.30$ for different temperatures: *a* – $T = 82$ K (*1*), 104 K (*2*), 153 K (*3*), 201 K (*4*), 333 K (*5*); *b* – $T = 140$ K (*1*), 170 K (*2*), 230 K (*3*), 273 K (*4*), 300 K (*5*).

As was mentioned above, it additional thermally activated dielectric permeability arises due to the electric dipole occurrence after jump of the electron from one well to another [3], [12], [16]–[18]. When the electron returns back to the first well (NP) in a time τ_m, the induced dipole disappears. The frequency region, where this additional polarization is observed, in accordance with the developed model depends on this time τ_m in the expression (2). As follows from the model [3], [12], [16]–[18], return of electron backward to the first well delays and is executed during $\tau_m \sim 10^{-3} - 10^{-6}$ s that is much longer than the time $\tau \sim 10^{-13}$ s. Therefore for the frequencies $f > f_{\min}$ (it coincides

with the position of f_1) the delay $2\pi f_1\tau_m$ of the returning jump can become greater than 2π, that creates the possibility for positive angles of the phase shifts θ and properly NC (inductive-like) effect.

As follows from the experimental results, in the as-deposited nanocomposite granular films $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(Al_2O_3)_{(1-x)}$ (set 1) and $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{(1-x)}$ (set 2) with $x \approx 0.30$ the best conditions (wider region of frequencies and higher temperatures) for the observation of NC effect (inductive contribution) are realised for the set 1 sample.

IV. CONCLUSIONS

The performed analysis have shown that positive angles of phase shifts observed in the samples studied, which are determined by specific *RLC* equivalent circuits, are due to the presence of a hopping mechanism in the carrier transport. As follows from the presented results, among the studied samples with $x \approx 0.30$ being of dielectric side of IMT the best conditions (wider region of frequencies and higher temperatures) for the observation of NC effect (inductive contribution) are realised for the sample $(Fe_{0.45}Co_{0.45}Zr_{0.10})_x(PZT)_{(1-x)}$.

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