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Determination of the conductive and structural characteristics of zirconium-containing amorphous nanogranulated composites from the microwave reflection coefficient

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Abstract. Amorphous nanogranulated composite films $((Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x})$ were studied experimentally. The film thickness, metal phase concentration, granules size, conductivity, and reflection coefficient of microwave waves at a frequency of 10 GHz were determined. A sequential algorithm for determining the conductive (grain conductivity) and structural (size of grains or gaps between granules, electron mean free path) characteristics from the measured microwave reflection coefficient for amorphous nanogranular composites is given. Using the algorithm and mechanism of intragranular currents based on experimental results, the conductivity of granules, the size of the gaps between the granules and the electron mean free path for zirconium containing series of films $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ were estimated. The dependences of the conductive and structural characteristics of the samples on the microwave reflection coefficient, the concentration of the metal phase and the effective thickness were obtained.

Keywords: Amorphous nanogranulated composite films, conductivity of granules, microwave reflection coefficient, mechanism of intragranular currents, electron mean free path

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Материалы конференции
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Определение проводящих и структурных характеристик цирконийсодержащих аморфных наногранулированных композитов по коэффициенту отражения СВЧ волн

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Аннотация. В работе приведен последовательный алгоритм для определения проводящих (проводимость гранул) и структурных (размеры гранул или промежутки между гранулами, длина свободного пробега электронов) характеристик по измеренному коэффициенту отражения СВЧ волн от цирконийсодержащих аморфных наногранулированных композитов. Используя механизм внутригранулярных токов, на основании результатов экспериментальных исследований коэффициента отражения СВЧ волн оценены проводимость гранул, размеры промежутков между гранулами и длина свободного пробега электронов для серий образцов $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ и $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$. Приведены зависимости проводящих и структурных характеристик от коэффициента отражения СВЧ волн, удельной проводимости композитов, а также эффективной толщины с учетом содержания металлической фазы.

Ключевые слова: Аморфные наногранулированные композитные пленки, проводимость гранул, коэффициент отражения СВЧ, механизм внутригранулярных токов, длина свободного пробега электронов

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Introduction

To create the latest small-sized microwave devices, nanostructured composites containing metal granules (for example, iron and cobalt) embedded in a dielectric matrix have been actively studied in recent decades [1–3]. The ferromagnetic metal in such composites causes a giant magnetoresistance [4] and a high level of absorption of microwave radiation [5]. Amorphous nanogranular composites containing zirconium, both in the metallic and dielectric phases, have a number of unique properties. For example, in [6, 7] for $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films, it was found that the dynamic conductivity in the microwave range can exceed the static conductivity measured at direct current by four orders of magnitude, long before the percolation threshold of the metal phase. It was shown in [8, 9] that the average granule size and the concentration of the metal phase of $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films determine not only the conductive but also the reflective properties of the films in the microwave range. In addition, the magnetic domain structure was visualized in the same films, which is an indicator of the presence of perpendicular magnetic anisotropy in the films and serves as evidence of percolation in the films.

A particularly significant factor is obtaining data about the properties of individual nanostructural elements based on the macroscopic properties of the entire object [10]. So, for modification and obtaining new conductive and structural properties of nanosized granular thin films, the most important parameters are the conductivity of one granule, the size of the granules and the gaps between these granules, and the mean free path of electrons. A numerical estimate of all the above parameters can be obtained based on knowledge of the conductive and reflective properties of the film.

The papers [11, 12] describe the mechanism of intragranular (intracluster) currents, which make the main contribution to the excess of dynamic conductivity over static one. In [13], methods of closed and open circuits of the mechanism of intragranular currents were proposed for calculating the conductive and structural characteristics of nanosized thin-film elements. These methods for describing the structural and conductive characteristics of amorphous granular composite films were tested [7, 10], in particular, on samples of $(Co_{45}Fe_{45}Zr_{10})_x(Al_2O_3)_{1-x}$.

In this work a sequential algorithm for determining the conductive and structural characteristics of amorphous nanogranular composites by means of the mechanism of intragranular currents (closed circuit method) using the size of granules and the reflection coefficient of microwave waves is presented. The gaps between the granules, the conductivity of the granules, and the mean free path of electrons were determined for a series of samples $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ and $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$.

Materials and Methods

Composite granulated films of composition $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ (thickness 535–1120 nm, $x \sim 0.27$–0.72) and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ (thickness 70–550 nm, $x \sim 0.25$–0.78) were obtained in a nitrogen atmosphere at a pressure of 0.024 and 0.080 Pa on a lavsan substrate

0.02 mm in thick. The films were fabricated by ion-beam sputtering at the Voronezh State Technical University. The film thicknesses were determined using a Tescan Vega LMH SEM from electron microscopic images of the cleavage end of the composite film. To determine quantitatively the elemental composition of the film surface, X-ray energy-dispersive spectrometry was used. The surface topography of the samples was studied using an Integra Prima atomic force microscope in semi-contact and contact modes. The reflection coefficient of microwave waves from thin films was measured in the frequency range 8–12 GHz. The device comprised a swept-frequency generator (SFG-61), a voltage standing-wave indicator with an attenuation module (YaSR-67), and a waveguide set of reflectometers. Standing-wave ratio dependencies on frequency were determined from directly on the indicator scale YaSR-67. The conductivity was obtained as the reciprocal of the resistivity measured at a dc current by the two-probe method with the use of the potentiometer substitution method.

Algorithm for determining conductive and structural characteristics

Let us consider a thin film composite with a nanogranular structure, in which the reflective properties due to the intrinsic conductivity of the granules. According to the closed circuit mechanism of the model of intragranular currents [11–13], the granule is included in a certain closed circuit, which due to the field of the primary wave contains an EMF source. The internal resistance of the source corresponds to the free space impedance. When an electromagnetic wave falls on a granular film, the electric field of the incident wave excites localized microwave currents inside the metal granules, which create a microwave magnetic field around themselves and form an electromagnetic wave reflected from the film. Due to the currents circulating in the conductive regions, the wave is re-emitted. The presence of conductive regions inside the film that are not in contact with each other increases the microwave reflection coefficient.

If the film consists of flat layers of identical cubic granules, the size of which is g, and the gaps between the granules p, then the reflection coefficient from the granular film at normal wave incidence is [10—15]:

$$R = \left(\left(\left(Z_0 + \frac{2(g+p)}{\sigma_g d g} \right) \frac{(g+p)}{\gamma g Z_0} \right)^{-1} \right)^2, \tag{1}$$

where σ_g is the conductivity of the granules, $\gamma = \exp(-p/g)$, d is the film thickness.

At $g >> p$ the film becomes continuous, $\sigma_g = \sigma$, and the reflection coefficient is determined by the well-known relation [10, 13—15]:

$$R = \left(\left(1 + \frac{2}{Z_0 \sigma d} \right)^{-1} \right)^2, \tag{2}$$

where σ is film conductivity.

To take into account the influence of the metallic phase on the reflection, we introduce the concept of an effective layer. This is the layer that contains only the metal phase in the composite. The thickness of such layer is [8, 13, 14]:

$$d_{\text{eff}} = d \cdot \frac{X, \text{at.\%}}{100\,\%}, \tag{3}$$

where X is the average value of the concentration of the metal phase for each sample (at.%). The effective layer consists of highly conductive granules, so the maximum thickness layer is able to reflect 95% or more of the total incident radiation. From relations (2) and (3) we determine the conductivity of the effective layer σ_{eff} at $R \geq 0.95$, which can be taken as the conductivity of the granules σ_g:

$$\sigma_{\text{eff}} = \frac{2}{Z_0 d_{\text{eff}}} \frac{\sqrt{R}}{1 - \sqrt{R}}. \tag{4}$$

Substituting the obtained values σ_g from (4) into (1), using the experimentally measured microwave reflection coefficient *R*, composite thickness *d* and granules size *g*, we determine the gaps between granules *p*. Solving (1) with respect to *g* and *p* we mathematically obtain four possible solutions [10]:

$$\left(g+p\right)_{1,2}=\frac{g}{4}\left(\sqrt{\frac{\sigma_g dZ_0\left(8\gamma\pm\sqrt{R}\cdot\sigma_g dZ_0\right)}{\sqrt{R}}}-\sigma_g dZ_0\right), \tag{5}$$

$$\left(g+p\right)_{3,4}=-\frac{g}{4}\left(\sqrt{\frac{\sigma_g dZ_0\left(8\gamma\pm\sqrt{R}\cdot\sigma_g dZ_0\right)}{\sqrt{R}}}+\sigma_g dZ_0\right), \tag{6}$$

of which only the first root gives non-negative values. Equations (5), (6) are solved numerically, since on its right side there is a coefficient γ, depending on *p*.

Finally, using the known relationship for conductivity [10,16]:

$$\sigma=\frac{n e^2 l}{p_F}, \tag{7}$$

where *e* is electron charge, *n* is concentration of conduction electrons in the film material, $p_F=2\pi\hbar\left(\frac{3n}{8\pi}\right)^{1/3}$ is boundary Fermi momentum, and solving (2) and (7) together, we determine the mean free path of electrons *l* depending on the measured reflection coefficient [10,13,16]:

$$l=\frac{4\pi\hbar}{n e^2 Z_0 d}\left(\frac{3n}{8\pi}\right)^{1/3}\frac{\sqrt{R}}{1-\sqrt{R}}. \tag{8}$$

Results and Discussion

The tables show the measurement results of metal phase concentration, thickness, reflection coefficient at 10 GHz, conductivity, sizes of granules and concentration of conduction electrons of amorphous composite films $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ (Table 1) and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ (Table 2). The values of the conduction electron concentration were obtained from the concentration dependences of the density of states at the Fermi level for various nanocomposites presented in [17].

Fig. 1 shows the experimental dependences of the reflection coefficient *R* on the concentration of the metal phase *X*. Fig. 2 presents dependences of the measured sizes of granules *g* on the effective layer thickness d_{eff}, and Figs. 3, 4 show calculated dependences of the gaps between the granules *p*, as well as the electron mean free path *l* on the measured reflection coefficient of microwave waves *R* of amorphous composite films $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$.

As can be seen from Fig. 1 at $X \leq 40$ at.% for $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ and $X \leq 60$ at.% for $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films the reflection coefficient is less than 1 % and does not depend on *X*. Further, as *X* increases, the reflection coefficient rapidly increases, and *R* for $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films 3–5 times higher than *R* for $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films in the metal phase concentration range of 60–70 at. %. Finally, in the interval $X \sim 70$–80 at.% values of the reflection coefficients are practically equalized and amount to 0.75–0.81. Note that at the same concentrations of the metallic phase, the thickness of the $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films is, on average, 2–2.5 times greater, and the conductivity is one–two orders of magnitude greater than for films $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ (Table 1, 2). Such differences in conductive and reflective properties are achieved due to the different structure of the films. If the effective layer with a maximum thickness of 429 nm for $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films and 780 nm for $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films (Fig. 2) consisted only of metal granules and reflected 95% and above of incident microwave radiation, then, according to relation (4), the conductivity of the granules is $4.76 \cdot 10^5$ S/m and $2.62 \cdot 10^5$ S/m, respectively. This value is only 4.5 times higher than the conductivity of the $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films and more than two orders of magnitude higher than the $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films. Therefore, at the same values of the reflection coefficient and thicknesses, the grain sizes for $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films are 3–4 times larger than for $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films, and the gaps between the granules are 2–3 times less (Fig. 2, 3). Note that, at the maximum R ~ 0.8, the gaps between grains for both films are no more than 2–5 nm. Therefore, the reflection from the film is determined precisely by the size of the granules, and the ratio of these sizes becomes close to the ratio of the conductivity of the granules (2.1 and 1.8, respectively).

Table 1

Metal phase concentration, thickness, reflection coefficient, conductivity, size of granules and concentration of conduction electrons of amorphous composite films $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$

Metal phase concentration X, at.%	Thickness d, nm	Reflection coefficient R	Conductivity σ, S/m	Size of granules g, nm	Concentration of conduction electrons $n\cdot10^{25}$, m^{-3}
27.1	570	$6.9\cdot10^{-4}$	3.35	20±2	$7.0\cdot10^{-3}$
32.3	610	0.00138	28.2	20±2	$4.2\cdot10^{-2}$
42.6	670	0.0146	119	19±2	1.3
48.3	670	0.186	1240	21±2	1.3
56.3	900	0.479	1930	22±2	1.3
56.8	711	0.589	2290	24±2	1.3
58.1	772	0.676	1890	23±2	1.3
60.2	697	0.749	6800	23±2	1.3
60.8	535	0.737	5300	20±2	1.3
61.2	900	0.577	2050	23±3	1.3
66.9	1030	0.729	3950	32±4	1.3
69.7	1120	0.791	57200	44±4	1.3
71.5	890	0.764	49700	25±4	1.3
71.9	1060	0.703	43400	38±4	1.3
72.5	900	0.746	57200	24±4	1.3

Table 2

Metal phase concentration, thickness, reflection coefficient, conductivity, size of granules and concentration of conduction electrons of amorphous composite films $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$

Metal phase concentration X, at.%	Thickness d, nm	Reflection coefficient R	Conductivity σ, S/m	Size of granules g, nm	Concentration of conduction electrons $n\cdot10^{25}$, m^{-3}
25	70	0.00154	0.030	33±3	$4.0\cdot10^{-3}$
38	190	0.00155	0.066	37±4	$3.2\cdot10^{-2}$
54	320	0.00157	0.91	70±8	1.3
59	280	0.00160	14.4	67±5	1.3
63	410	0.166	25	83±7	1.3
65	400	0.250	106	84±7	1.3
68	420	0.591	1000	86±7	1.3
73	390	0.562	712	79±8	1.3
77	530	0.790	3012	92±8	1.3
75	470	0.649	3820	90±9	1.3
78	550	0.810	4410	95±9	1.3
77	420	0.753	4240	89±8	1.3

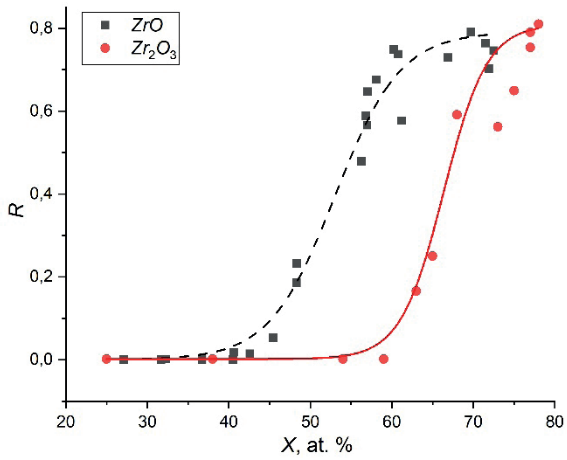

Fig. 1. Dependences of the reflection coefficient on the content of the metal phase

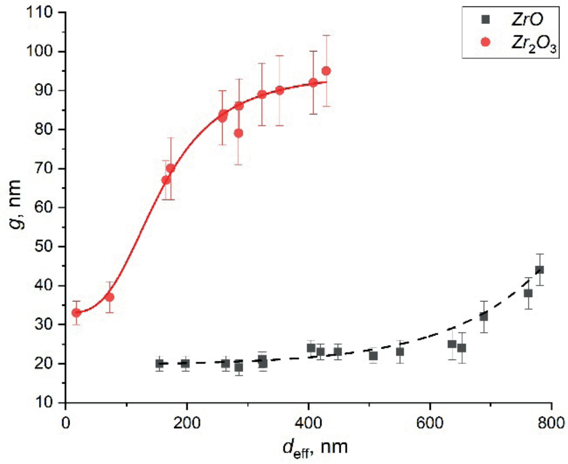

Fig. 2. Dependences of grain sizes on effective film thickness

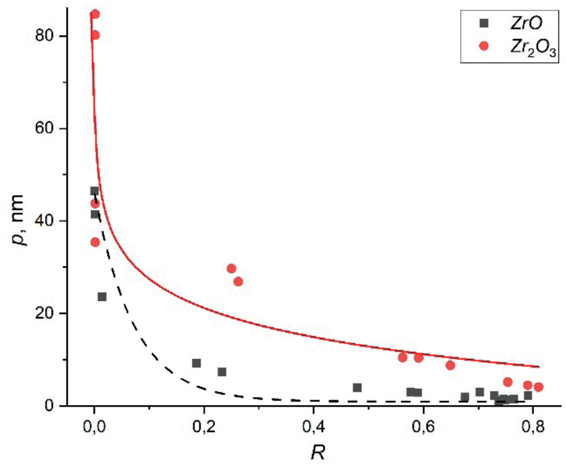

Fig. 3. Dependences of the gaps between the granules on the reflection coefficient

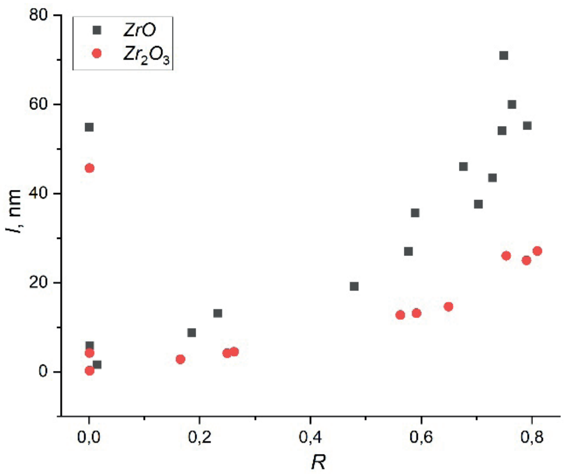

Fig. 4. Dependences of the electron mean free path on the reflection coefficient

From Fig. 4 it can be seen that the mean free path generally increases with the increase in the reflection coefficient. In this case, for $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films at R = 0.48–0.70, the mean free path, taking into account the statistical spread, coincides with the grain size. At reflectance values above 0.70, l exceeds the granule size 2–2.5 times. For $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ films on average, the mean free path of electrons is 1.5–2 times less than for $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ films for the same R.

Conclusion

The paper presents the results of experimental studies of the thickness, concentration of the metal phase, microwave reflection coefficient, conductivity and grain sizes of amorphous nanogranular composite films $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$. Using the closed circuit mechanism of the model of intragranular currents, an algorithm for calculating the conductive and structural characteristics of composites from the measured reflection coefficient is proposed. Using the above algorithm, the results of calculations of the conductivity of granules, gaps between granules and the mean free path of electrons for films $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ and $(Co_{45}Fe_{45}Zr_{10})_x(Zr_2O_3)_{1-x}$ were determined. The dependences of the conductive and structural characteristics on the reflection coefficient of microwave waves and the effective thickness of the films are obtained, taking into account the concentration of the metal phase.

REFERENCES

1. **Vendik I.B, Vendik O.G.**, Metamaterials and their application in microwaves: A review, Tech. Phys. 1(58) (2013) 1–24.

2. **Zolotukhin I.V., Kalinin Yu.E., Ponomarenko A.T., Shevchenko V.G., Sitnikov A.V., Stognei O.V., Figovsky O.**, Metal-dielectric nanocomposites with amorphous structure, J. Nanostructured Polymers and Nanocomposites. 1(2) (2006) 23–34.

3. **Kalinin Yu.E., Remizov A.N., Sitnikov A.V.**, Electrical properties of amorphous $(Co_{45}Fe_{45}Zr_{10})_x(Al_2O_3)_{1-x}$ nanocomposites, Phys. Solid State. 11(46) (2004) 2146–2152.

4. **Gerber A., Milner A., Groisman B., Karpovsky M., Gladkikh A., Sulpice A.**, Magnetoresistance of granular ferromagnets, Phys. Rev. B. 10(55) (1997) 6446–6452.

5. **Kazantseva N.E., Ponomarenko A. T., Shevchenko V.G., Chmutin I.A., Kalinin Yu.E., Sitnikov A.V.**, Phys. and chem. of mater. treat. 1 (2002) 5–11.

6. **Antonets I.V., Kotov L.N., Kalinin Yu.E., Sitnikov A.V., Shavrov V.G., Shcheglov V.I.**, Dynamic Conductivity of Amorphous Nanogranular Films in the Microwave Frequency Range, Tech. Phys. Lett. 7(40) (2014) 584–586.

7. **Antonets I.V., Kotov L.N., Kirpicheva O.A., Golubev E.A., Kalinin Yu.E., Sitnikov A.V., Shavrov V.G., Shcheglov V.I.**, Static and Dynamic Conduction of Amorphous Nanogranulated Metal–Dielectric Composites, J. of Communications Technology and Electronics. 8(60) (2015) 904–914.

8. **Antonets I.V., Kotov L.N., Golubev Ye.A.**, Influence of composition and nanogranular structure of (Co+Fe+Zr)/(ZrO) composite films on conductivity and microwave reflective properties, Mater. Chem. and Phys. 240 (2020) 122097.

9. **Antonets I.V., Kotov L.N., Golubev E.A., Kalinin Yu.E., Sitnikov A.V.**, The structure, conductive properties, and reflective properties of amorphous granulated $(Co_{45}Fe_{45}Zr_{10})_x(ZrO)_{1-x}$ composite films, Tech. Phys. 2(62) (2017) 261–269.

10. **Antonets I.V., Golubev E.A., Shcheglov V.I.**, Algorithm for determining the structural characteristics of amorphous nanogranulated composites from the microwave waves reflection or conductivity, Mater. Chem. and Phys. 290 (2022) 126533.

11. **Antonets I.V., Kotov L.N., Kirpicheva O.A., Golubev E A., Kalinin Yu.E., Sitnikov A.V., Shavrov V.G., Shcheglov V.I.**, Dynamic conductivity mechanism in amorphous nanogranulated "metal-dielectric" films in microwave frequencies, J. of Radio Electronics. 4 (2014) (electronic journal). http://jre.cplire.ru/jre/apr14/12/abstract_e.html

12. **Antonets I.V., Kotov L.N., Golubev E.A., Shavrov V.G., Shcheglov V.I.**, Dynamic conductivity of nanogranulated films "metal-dielectric" on the microwave frequencies, J. of Radio Electronics. 5 (2018) (electronic journal v. 5). http://jre.cplire.ru/jre/may18/2/abstract_e.html

13. **Antonets I.V., Golubev E.A., Shcheglov V.I., Kotov L.N.,** Closed and open circuit methods for calculating the conductive and structural characteristics of thin-film elements by the reflection coefficient of microwave waves, AIP Conf. Proc. 2467 (2022) 00009.

14. **Antonets I.V., Golubev E.A., Shcheglov V.I., Sun S.**, Electromagnetic shielding effectiveness of lightweight and flexible ultrathin shungite plates, Current Appl. Phys. 29 (2021) 97–106.

15. **Golubev Ye.A., Antonets I.V., Shcheglov V.I.**, Static and dynamic conductivity of nanostructured carbonaceous shungite geomaterials, Mater. Chem. and Phys. 226 (2019) 195–203.

16. **Antonets I.V., Kotov L.N., Nekipelov S.V., Shavrov V.G., Shcheglov V I.**, Electrodynamic properties of thin metal films with different thicknesses and morphologies of the film surface, J. of Communications Technology and Electronics. 10(49) (2004) 1164–1170.

17. **Sitnikov A.V.**, Electrical and magnetic properties of nanoheterogeneous metal-dielectric systems. PhD thesis. Voronezh: VSTU, 2010.

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