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Percolation Phenomena in $Cu_x(SiO_y)_{100-x}$ Nanocomposite Films Produced by Ion Beam-Sputtering

T.N. Koltunowicz[a]*, P. Zukowski[a], K. Czarnacka[a], I. Svito[b] and A.K. Fedotov[b]

[a]Department of Electrical Devices and High Voltage Technology, Lublin University of Technology, Nadbystrzycka 38a, 20-618 Lublin, Poland

[b]Belarusian State University, 4 Nezavisimosti Av., 220030, Minsk, Belarus

In this paper the results of examinations of nanocomposites $Cu_x(SiO_y)_{100-x}$ produced by ion beam sputtering using argon ions were presented. The examinations were performed by the use of ac devices for measuring frequency in the range 50 Hz–1 MHz and temperatures from 81 K to 273 K. The measurements were performed for the samples directly after production. Based on temperature dependences of conductivity σ, which were determined at the frequency 100 Hz, the Arrhenius graphs were prepared. From these graphs conductivity activation energies ΔE were calculated. Dependences of conductivity and activation energy of electrons on the metallic phase content x at the frequency 100 Hz were determined. Analysis of the obtained dependences shows that conductivity is a parabolic function of the metallic phase content x in nanocomposites. Changes of activation energies of nanocomposites, in which metallic phase contents are in the ranges $x < 12$ at.% and $x > 68$ at.%, demonstrate negative values — metallic type of conductivity. In the range 12 at.% < x < 68 at.% activation energies have positive values — the dielectric type of conductivity. It was established that for the metallic phase content of about 68 at.% the real percolation threshold occurs, and the conduction changes from dielectric to metallic type.

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1. Introduction

Nowadays many papers are devoted to examinations of granular nanocomposites in the form of thin layers or coatings [1–3]. When the material structure is miniaturized to the nanometer scale, its properties are changed in relation to those that material had in the macroscale [4]. Such materials could demonstrate a memory shape memory effect [5] or interesting magnetic properties [6, 7] and magnetotransport [8].

Examinations of electric properties on ac of granule nanocomposites with metal–dielectric structure, which contain nanoparticles of ferromagnetic metallic phase $Co_{45}Fe_{45}Zr_{10}$ in the matrices Al_2O_3 [9], PZT [10, 11] or CaF_2 [12], prepared by ion methods [13–16] demonstrate that in those materials noncoil-like inductance, voltage resonance and, in certain cases, current resonance, characteristic of conventional serial and parallel RLC circuits [17, 18] occur.

An important aspect is the fact that electric properties of the nanocomposites depend on the amount and size of metallic phase nanoparticles, type of interaction and creation of transition phases at the metal–dielectric interface. Metallic phase nanoparticles, when separated by the dielectric barrier create single potential wells and, depending on the atmosphere composition, they can be additionally surrounded by a layer of the metallic phase oxides [19, 20]. Metallic phase particles can also form as nanodimensional rods [21]. These phenomena determine the type of electric charges transport mechanism in nanomaterial. Nanocomposites properties also depend on nanolayers annealing in adequate temperatures [22].

Changes in properties of granular nanocomposites occurring with a change in the content of the metallic phase x are described by percolation theory [23]. Critical content of the metallic phase in dielectric, at which material changes type of conduction from the dielectric type to metallic one, is called the percolation threshold x_c. It was assumed that a given group of nanocomposites ranked by the content x is divided into three sections: under the percolation threshold when $x < x_c$, near the threshold when $x \approx x_c$ and above the percolation threshold when $x > x_c$ [4].

In the previous works concerning nanocomposites with the dielectric matrix in the form of SiO_2 with nanoparticles of metallic phase Cu, it was determined that the ion-beam sputtering process has impact on the matrix chemical composition [24]. In the paper [25] the changes of matrix chemical composition for metallic phase Cu nanoparticles content within the range 9.6 at.% < x < 72.9 at.% were determined. Therefore there was introduced new nomenclature which includes the variability of oxygen content in the matrix for different metallic phase x content. A hopping conduction model was also proposed for this type of material [25].

The aim of the paper was to determine the changes of conductivity measured on ac and electrons activation energy in dependence on the metallic phase content of nanocomposite $Cu_x(SiO_y)_{100-x}$.

2. Experimental results and discussion

The object of research were nanocomposite $Cu_x(SiO_y)_{100-x}$ samples, prepared by ion-beam

*corresponding author; e-mail: t.koltunowicz@pollub.pl

sputtering in argon atmosphere with the pressure 4×10^{-3} Pa according to the method described in [26, 27]. The samples with the metallic phase content x from 9.6 at.% to 72.9 at.% were examined directly after preparation (nonannealed samples). For checking the stoichiometry of the samples the X-ray microanalysis was used with an accuracy of $\sim 1\%$ [25].

Temperature ac measurements of electrical parameters in the range 81–273 K were performed with the use of device described in [28]. The current's frequency was changed in the range 50 Hz–1 MHz.

In Figs. 1 and 2 the frequency dependences on conductivity σ for different metallic phase contents x and selected measurement temperatures T_p are presented. For the samples with the contents $x < 11.6$ at.% and $x > 69.1$ at.% temperature dependences of conductivity are poor, and conductivity values decrease with the measurement temperature increase (Fig. 1), which is characteristic of metallic type of conduction.

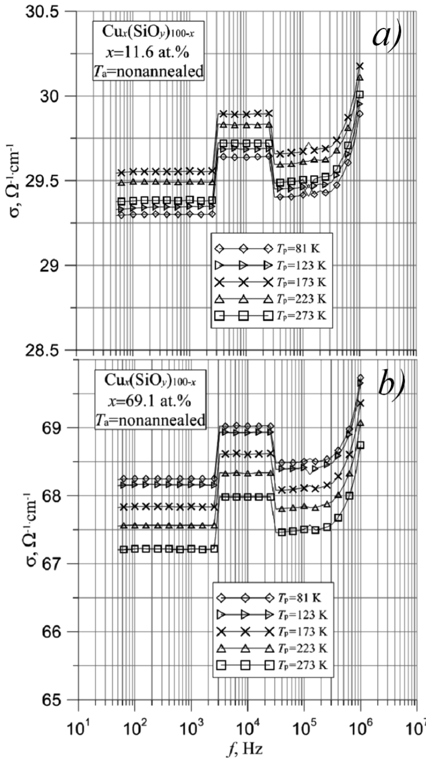

Fig. 1. Plots of conductivity σ dependence on measurement temperature T_p and measurement frequency f of nanocomposite $Cu_x(SiO_y)_{100-x}$ with metallic phase: (a) $x = 11.6$ at.%, (b) $x = 69.1$ at.%.

For the samples with the metallic phase content 11.6 at.% $< x <$ 69.1 at.% the conductivity value increases together with the measurement temperature. It means that the dielectric type of conduction occurs in them. Strong temperature dependence on conductivity occurs for the samples with the Cu content equal 30 at.% and 35 at.% (Fig. 2).

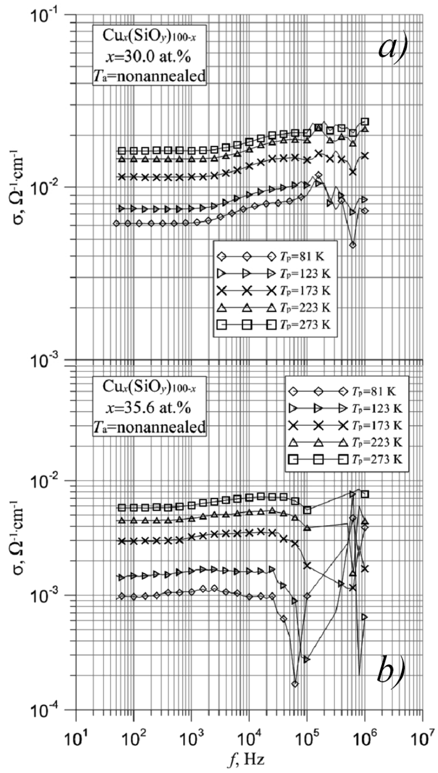

Fig. 2. As in Fig. 1, but for (a) $x = 30.0$ at.%, (b) $x = 35.6$ at.%.

In Fig. 3 the dependence of conductivity, measured at the frequency 100 Hz for selected measurement temperatures, on metallic phase content is presented. As can be seen from this figure, change x from about 10 at.% to about 30 at.% causes conductivity decrease by almost 5 orders of magnitude. A further increase in the concentration of metallic phase to about 73 at.% causes sharp increase in conductivity. Based on the temperature dependences on conductivity, the Arrhenius graphs for the frequency $f = 100$ Hz were prepared, from which electrons activation energies were calculated.

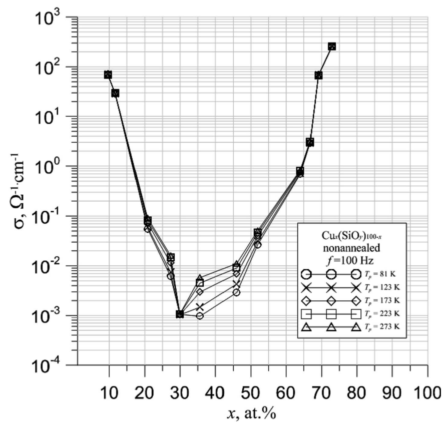

Fig. 3. Plots of conductivity σ dependence on metallic phase content x at the frequency $f = 100$ Hz for different measurement temperatures.

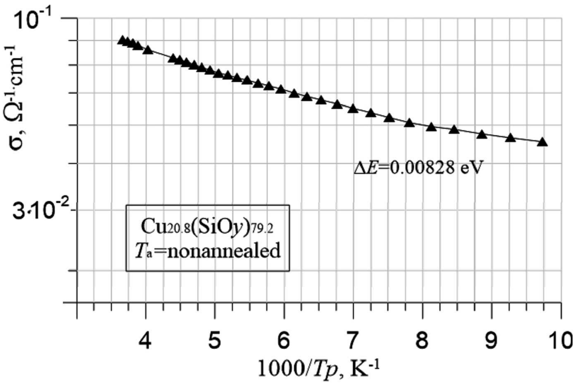

Fig. 4. Arrhenius graph of conductivity σ for nanocomposite $Cu_{20.8}(SiO_y)_{79.2}$ at the frequency $f = 100$ Hz.

In Fig. 4 an example of the Arrhenius graph and determined activation energy value $\Delta E = 0.00828$ eV is presented.

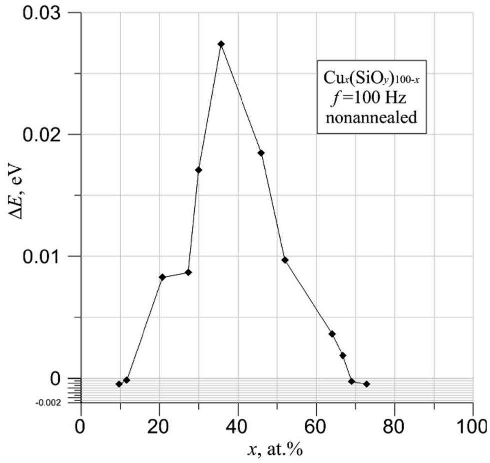

Fig. 5. Plots of activation energy of electrons ΔE dependence on metallic phase content x for nanocomposite $Cu_x(SiO_y)_{100-x}$ at the frequency $f = 100$ Hz.

The values ΔE for every sample of nanocomposite $Cu_x(SiO_y)_{100-x}$ are presented on the graph, which is shown in Fig. 5. As can be seen in the graph, electrons activation energies for nanocomposites, for which metallic phase contents x are in the ranges $x < 12$ at.% and $x > 68$ at.%, have negative values. In this case a metallic type of conduction takes place. In the interval 12 at.% $<$ x $<$ 68 at.% activation energies ΔE have positive values which corresponds to the dielectric type of conduction. It means that the examined materials have two percolation thresholds — first at about 12 at.% — unusual for the nanocomposites and percolation mechanism transit from the metallic type of conduction to the dielectric one together with metallic phase increase, and second at about 68 at.% — typical of percolation transit from the dielectric type of conduction to the metallic one.

It is hard to imagine what form should be copper in, when $x < 12$ at.%, metallic phase nanoparticles form conductive chains. It seems that copper with the content in the range $x < 12$ at.%, is present in the matrix SiO_2 in the form of single atoms or small clusters, containing several to tens of atoms. Such a high concentration of single copper atoms or their small clusters causes creation of doped band in the forbidden energy band of silicon dioxide, in which valence electrons are located. Copper atoms or their clusters, in this case, serve as a dope function, causing metallic type of conduction, similar to that observed in depleted semiconductors. This conduction takes place via the transfer of electrons located in the doped band in the electric field.

Together with the increase of x above 12 at.% nanoparticles start to grow rapidly, their number rapidly reduces, and conductivity changes from band conduction to hopping, characteristic of nanocomposites metal–dielectric at the dielectric side [4]. In this case nanoparticles are separated by the dielectric barrier of matrix material SiO_2, and activation energies obtain positive values. The increase of copper content above 68 at.% leads to the situation when nanoparticles, due to high concentration, contact with each other forming conductive chains. In this case conductivity has metallic character, which can be seen from the temperature dependence of conductivity (Fig. 1) — the decrease of conductivity value together with the temperature increase.

3. Conclusions

It was established that in the nanocomposite $Cu_x(SiO_y)_{100-x}$ with a low copper content ($x < 12$ at.%) a dopant band is created in the forbidden band of silicon dioxide, in which valence electrons of copper atoms are located. It causes metallic type of conduction, similar to that observed in the depleted semiconductors.

Together with the x increase above 12 at.% metallic phase nanoparticles are formed, and conduction transform from banding (metallic type) to hopping, characteristic for nanocomposites metal–dielectric at the dielectric side. Nanoparticles are separated by the dielectric barrier of matrix material SiO_2, and activation energy of conductivity reaches positive values.

For the metallic phase content of about 68 at.% the real percolation threshold occurs, and the conduction changes from the dielectric to metallic type.

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