

**SUPRAMOLECULAR ASSEMBLIES OF CONFIGURATION INORGANIC SEMICONDUCTOR/OLIGOMER****I.I. Grygorchak, D.V. Matulka, F.O. Ivashchyshyn, O.S. Zaichenko,  
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The possibility of formation of such supramolecular complexes as inorganic semiconductor/oligomer with use of intercalation technologies is presented in this work. Lamellar semiconductors gallium selenide and indium selenide were objects of research. These compounds were used as the body of host. Molecules of oligomer oligo-dimethylamino-methacrylate were used as guest component. The results of research are represented with using the method of impedance spectroscopy.

**Keywords:** intercalation, semiconductors InSe and GaSe, oligomer, oligo-dimethylamino-methacrylate, impedance spectroscopy.

В роботі представлена можливість створення за допомогою інтеркаляційних технологій складних супрамолекулярних комплексів – неорганічний напівпровідник/олігомер. Досліджувались шаруваті напівпровідники селенід галію та селенід індію, які слугували матрицею-“господарем”. В якості “гостьового” компонента використовувалися молекули олігомеру – оліго-диметиламіно-метакрилат. Представлені результати досліджень виконаних з допомогою методу імпедансної спектроскопії.

**Ключевые слова:** інтеркаляція, напівпровідники InSe та GaSe, олігомер, оліго-диметиламіно-метакрилат, імпедансна спектроскопія.

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**INTRODUCTION**

The fundamental collisions between the functionality of traditional nanomaterials and nanostructures on their basis and rapid development of nanotechnology (quantum coherent spintronics, nanophotonics) and current tasks of autonomous power (a over high capacitive nanogenerators and supercapacitors) were forced paid increased attention to the supramolecular structures as objects of which are often associated possibility of unique physical and chemical properties, in part – paradoxical. Today actually, new principle of organization of matter – clathrate is one of their varieties.

Receptor (“host”) contains the molecular centers that are set up selective binding of a defined substrate (“guest”) by the so-called “lock-key” in all supramolecular assemblies. The principle of complementarity (geometric, topological and charge corres-

pondence) of the “guest-host” is one of the most important in such systems.

Intercalation concept of forming supramolecular assemblies that recommended by us can serve as an important step in the development of this direction of research materials – “hosts” that are used for this purpose can “recognize” guest component at thermodynamic complementarity, as result by forming the corresponding guest degrees of freedom can modified its structure. Such approach does not only increase the variability of synthetic supramolecular systems, but also opens the possibility of forming hierarchical fractal supramolecular architectures. It is expected that the latter will open new opportunities nanoengineering, launching, first, a new area of technology such as supramolecular photoelectronics [1 – 3].

However, the progress made along the way, cannot be considered impressive. There's very little accumulated experience and made only the first steps [4 – 6]. An attempt to fill the gap in some measure of that field of research is the purpose of this paper.

## CONCEPTIONS AND EXPERIMENTAL

The layered semiconductors gallium selenide (GaSe) and indium selenide (InSe) were served as the basic object (“host” material) in the experiments. Crystals were grown by Bridgman-Stokbarhera and possess pronounced layered structure, *p* and *n*-type conductivity, respectively. Band gap (from optical data) for the first type of single crystal was 2.02 eV and 1.22 eV – for the second. As is well known [7, 8], they are characterized by the presence of so-called “guest” positions. Such positions are oriented perpendicular to the crystallographic axis *C* domains where actions of weak van der Waals forces. Inclusion to the designated intracrystallite intervals of alien ions, atoms or molecules is known as intercalation phenomenon [9]. These materials have features of the crystal structure which do not require precision mechanical treatment and chemical surface treatment that cause its increased inertia to absorb foreign atoms or molecules. The absence of broken bonds on their surfaces provides to very low surface recombination velocity. Additionally, they are characterized by high photosensitivity in the visible spectrum.

On the other hand, in present time oligomer such as oligo-dimethylamino-methacrylate (ODM) is well known as receptor of metal cations. Because it directly neither GaSe, not InSe does not implement, then the formation intercalation GaSe <ODM> and InSe <ODM> was applied next three-stage scheme of “crystal engineering” (fig. 1). Sodium nitrite is introduced in the original matrix by direct exposure of its fusion semiconductor single crystal at a temperature of 3000 °C during 5 ÷ 10 minutes on the first stage. As a result, of the *n*-stage ordering [10, 11] the distance between appropriate layers significantly increases.

The next step was deintercalation of sodium nitrite from crystals by its extraction during five times the 24-hour cycle and drying under low pressure at a temperature of 110 °C. Deintercalation matrix at the expense of weakened van der Waals contacts and modified intracrystallite force fields were suitable for implementation oligomeric guest component.

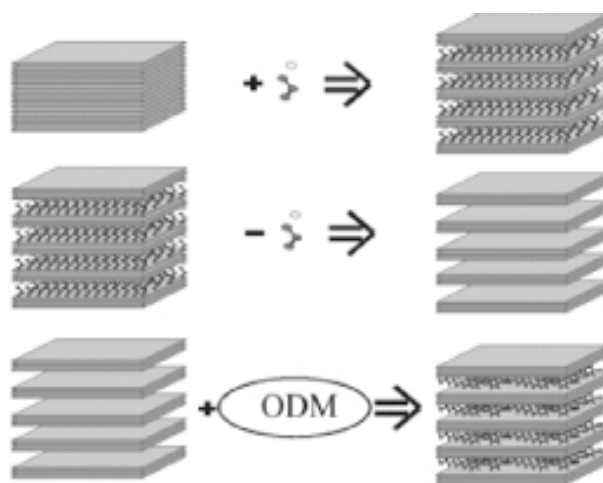


Fig. 1. Stages of formation of hybrid multilayer GaSe <ODM> and InSe<ODM> nanostructures.

Therefore, the third stage was carried out as intercalation oligo-dimethylamino-methacrylate (it structure is representing on fig. 2) and cointercalation lithium with him in extended lattice.

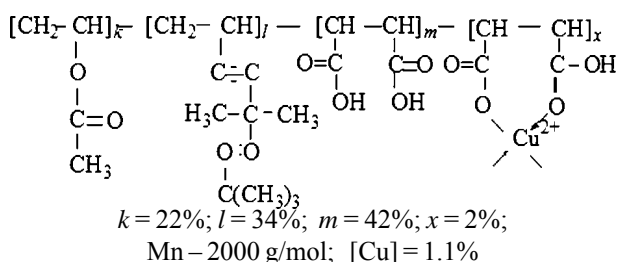


Fig. 1. Structure of oligoperoxide metal complexes (OMK)

This process was conducted in three stages:

- on the first stage, the extended matrix was modified by the oligoperoxide metal complex by sorption (OMC) for this purpose it was submerged in 1% solution of OMC in ethanol (5 ml) and was kept there during 10 min. The matrix was washed thoroughly with pure ethanol and dried after following the modification.
- on the second stage, incultation of polymers had taken place. Modified extended crystal was submerged in 2% solution dimethylaminoethyl methacrylate ((CH<sub>2</sub> = C(CH<sub>3</sub>)COOCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, DMAEM) in water and was kept at 40 °C within 4 hours. The modified crystal carefully washed with distilled water and ethanol after polymerization;
- modified extended crystal was submerged in a solution of 1 M lithium boron fluoride in  $\gamma$ -Butyrolactone after forming the of polymer layers-poliDMAEM and kept there within 8 hours, then single crystal was washed with ethanol and dried.

X-ray study of the obtained nanostructures were carried out on X-ray diffractometer DRON-3 CoK $\alpha$  emission that monochromated by hammering from the plane (200) single crystal of LiI.

Impedance measurements in the direction of crystallographic axis C were performed in the frequency range from  $10^{-2}$  to  $10^5$  Hz by measuring complex "AUTOLAB" "ECO CHEMIE" (The Netherlands) Company, which was equipped with computer programs FRA-2 and GPES. Frequency dependence of complex impedance Z was analyzed by using graph analysis software package ZView 2.3 (Scribner Associates). Error of approximation did not exceed 4%.

## RESULTS AND DISCUSSION

Fig. 3 shows x-ray diffraction of the gallium selenide before and after intercalation oligo-dimethylamino-methacrylate. It should be noted that after intercalation intensity of reflexes falls (eg., in the vicinity  $2\Theta = 25.9$  in near 4 times) than of the angular vicinity  $2\Theta = 55$ , where it has doubled after intercalation. It should be noted that the increase ODM number of intense reflections in the range of diffraction angles  $2\Theta = 5 \div 120$  degrees after intercalation. This small-angles reflexes ( $2\Theta = 11.1$  and  $2\Theta = 22$ ) shifted to the small-angle region relative to the original matrix reflections ( $2\Theta = 13.3$  and  $2\Theta = 25.9$ , respectively), and large-angle ( $2\Theta = 70.8$  and  $2\Theta = 85$ ) in the large-angle. All this indicates that structure has fundamentally changed due to intercalation of gallium selenide oligo-dimethylamino-methacrylate.

As has turned out, the processes of the current passing normally to nanolayers which received hete-

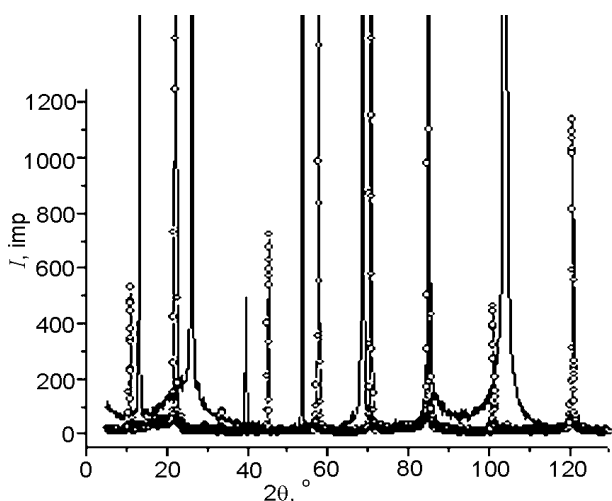


Fig. 3. X-ray diffractograms of GaSe before (solid line) and after (line with circles) introduction of oligo-dimethylamino-methacrylate.

rophase of nanohybride structures are significantly depend against the degree of expansion of the original crystal lattice along the crystallographic axis C. Fig. 4a and 4b are presents the frequency behavior of the real part of the specific impedance, which measured normally to the planes of nanolayers of GaSe <ODM> ( $\rho(\omega)$ ) with different degree of expansion. For the original 2- and 4-times enhanced matrix dependences  $\rho(\omega)$  has accustomed manner: low frequency branches go into falling at high frequencies due to the contribution of hopping conduction in localized states near the Fermi level, or excitation processes capture them in the tail areas or delocalized band states [12 – 14]. However, we should pay attention to the following unusual aspect such as a strong deformation of low branches  $\rho(\omega)$ , while it has huge growth.

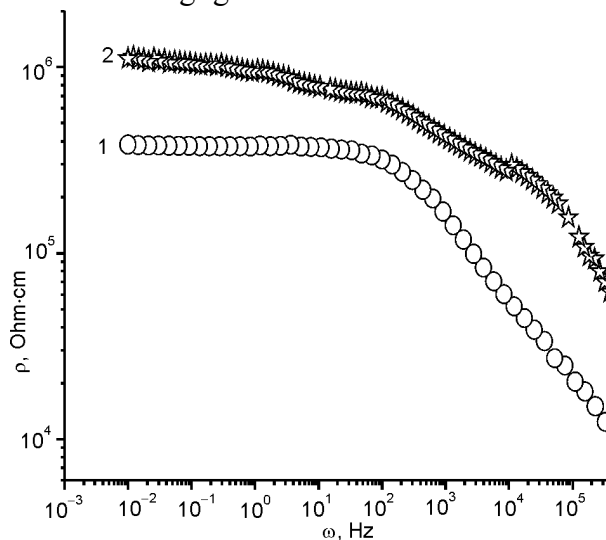


Fig. 4a. Frequency dependence of the real part of complex specific impedance, normally to the layers doubly expanded GaSe matrix (1) and GaSe <ODM> nanostructures on the its basis – (2).

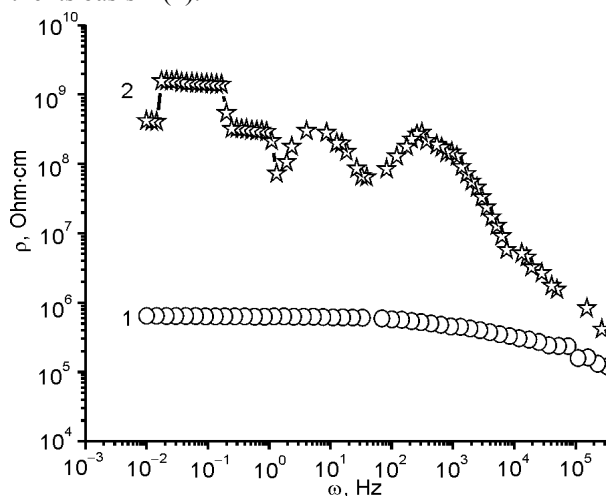


Fig. 4b. Frequency dependence of real part of complex specific impedance, normally to the layers expanded four-fold GaSe matrix (1) and GaSe <ODM> nanostructures on the its basis – (2).

Nyquist diagrams which built in the complex plane of the depending imaginary part of impedance ( $-Z''$ ) from its real part ( $Z'$ ) have unusual character. They radically transformed has compared with the original expanded matrix. The first thing can be seen that after the implementation of ODM of the two times expanded matrix Nyquist diagram transformed from single arc character (which reflects the capacitive response of the localized states and the properly frequency dependent impedance) to the clearly defined three arc impedance (curve 2, fig. 5a). The formation of energy relief after the implementation of ODM is suggests by this character of Nyquist diagram. Three potential barriers have made significant contribution in the energy relief. The first of barriers (the most high frequency) associated with the original matrix, the second related with layers of organic content, and the most low frequency arc displays process of current passing through the interfacial boundaries of inorganic semiconductor and oligomer.

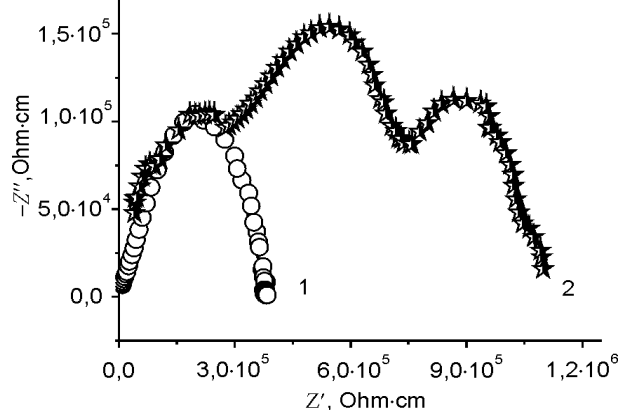


Fig. 5a. Nyquist diagrams were constructed for the normally direction to the layers GaSe matrix doubly expanded (1) and GaSe <ODM> nanostructures on its basis – (2).

Correspondence between the deformation of low branches ( $\omega$ ) and the transition of the related branch of Nyquist diagrams in IV-”inductive” quadrant of the complex plane (fig. 5b) has observed at entering oligomer for fourth times expanded matrix of GaSe. In general, the phenomenon of “negative” capacitance is sufficiently well known from the literature, although its mechanism is not completely elucidated, and perhaps it does not have the same nature [15, 16]. For the most common mechanism, inductive behavior occurs even when the charge is introduced in small layers or sub dimensions, i.e., the range of several nanometers [17]. The inductive response in medium frequency range which is a rare event we observe in this case.

The current-voltage characteristics of GaSe <ODM> along the crystallographic axis C have

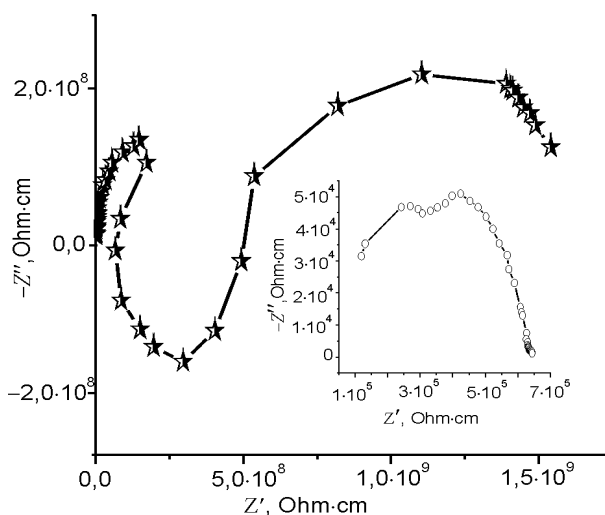


Fig. 5b. Nyquist diagrams were constructed for the perpendicular direction to the layers GaSe matrix expanded in four times (inset to figure) and GaSe <ODM> nanostructures on its the basis.

typical hysteresis for both stages of decomposition, but their appearance is strongly depends on them (fig. 6a, 6b).

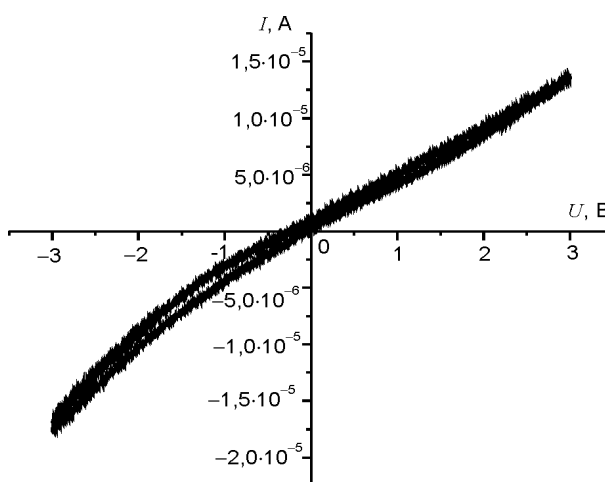


Fig. 6a. Current-voltage characteristic, was built for the perpendicular direction to the layers GaSe <ODM> nanostructures doubly expanded.

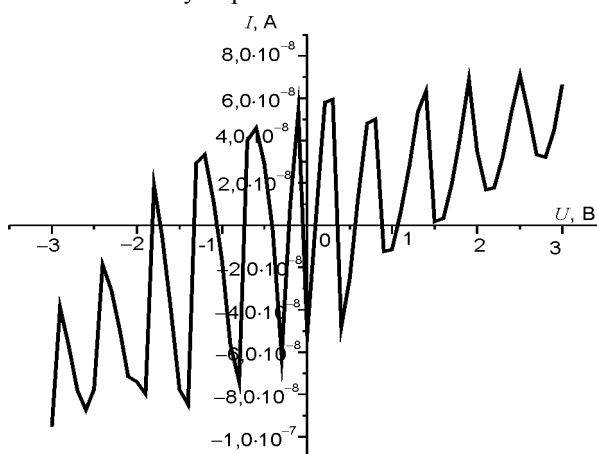


Fig. 6b. Current-voltage characteristic, was built for the perpendicular direction to the layers GaSe <ODM> nanostructures in four times expanded.

Polarization characteristics are unusual and depend on the degree of splitting. Foremost, we note that the nanostructure obtained from matrix doubly expanded the loss tangent is higher than the unit in the investigated frequency range and is not interesting in terms of capacitor building. Maintaining frequency genesis gallium selenide doubly expanded the relative permittivity reduced in four times while after the introduction of. The situation is significantly different for nanostructures obtained from the expanded four-fold matrix. As shown in fig. 7a, 7b in this case we have reduce of the loss tangent and relative permittivity on three orders (to a value less than 10) after introduction of the oligomer and the emergence of high-frequency oscillations of the relative permittivity.

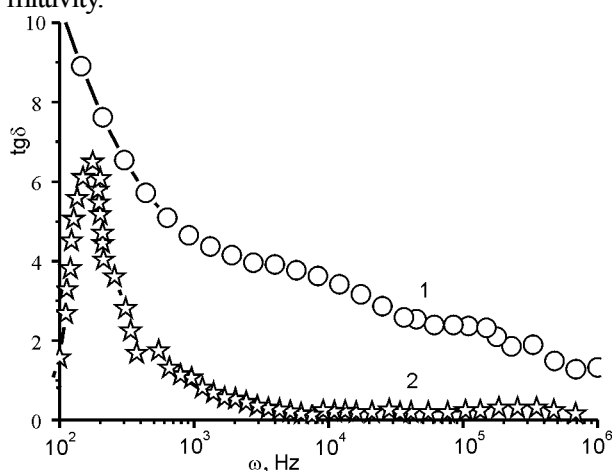


Fig. 7a. Frequency dependence of loss tangent, perpendicular to the layers GaSe matrix expanded in four times (1) and GaSe <ODM> nanostructures on the its basis - (2).

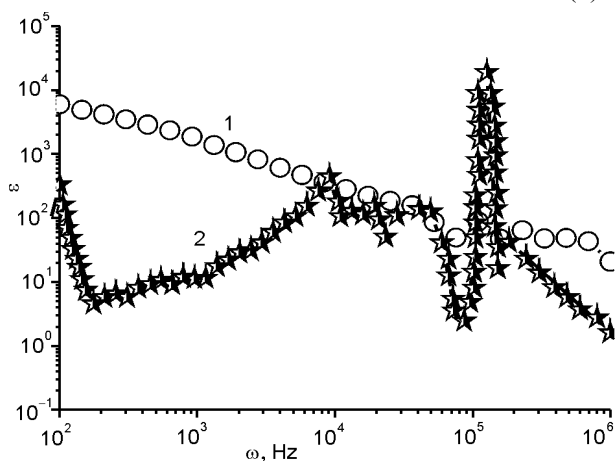


Fig. 7b. Frequency dependence of the dielectric constant perpendicular to the layers GaSe matrix expanded in four times (1) and GaSe <ODM> nanostructures on the its basis - (2).

Fig. 8 is shown the frequency behavior of the real part of the specific impedance, normally to the InSe <ODM> planes nanolayers with different degree of expansion, which, is weakly frequency

dependent. Increase expansion degree of the original crystalline InSe matrix leads to the reduce ρ(ω). Probably this is due an increase in the relative content of oligomer layers that serve as well conductance “bridges” between the individual layers of the expanded matrix.

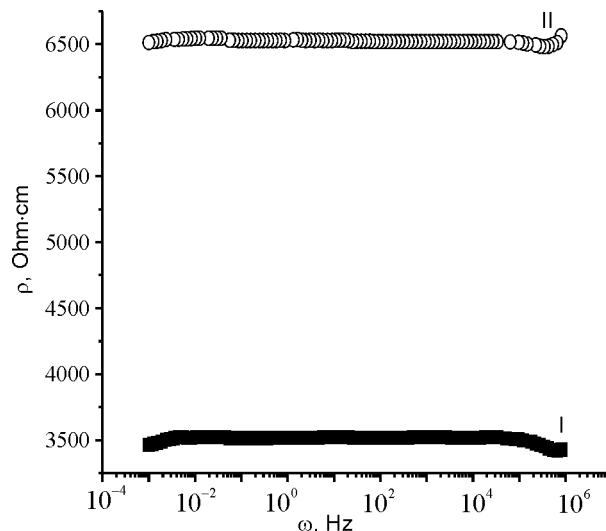


Fig. 8. Frequency dependence of the real part of the complex specific impedance, perpendicular to the layers of InSe <ODM> nanostructures with expansion degree 2 - (II) and 4 - (I).

For a more detailed identification of the nature of the frequency behavior of ρ(ω) let we analyze the Nyquist diagrams are shown in fig. 9. As you can see, the impedance hodograph has represented a line almost parallel to the axis values of the imaginary part of complex impedance with the exception of the most low frequency δ-vicinity. This behavior is outside the specified vicinity with high

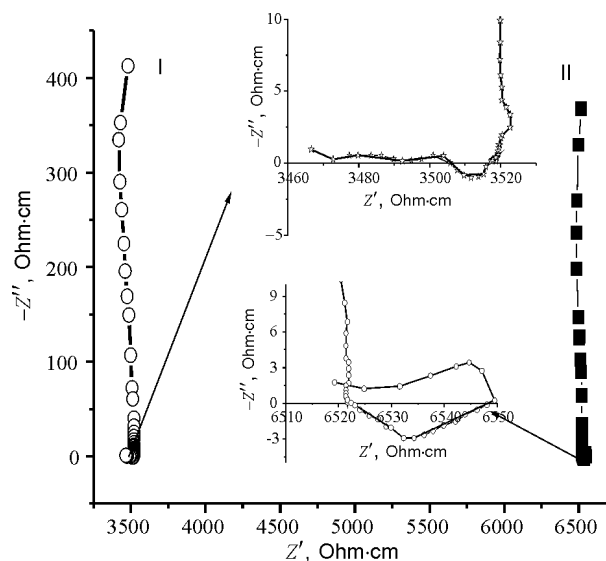


Fig. 9. Nyquist diagrams for the perpendicular direction to the layers of InSe <ODM> nanostructures with expansion degree 2 - (II) and 4 - (I).

precision modeled by series connected resistor and capacitor, for the most low frequency  $\delta$ -vicinity situation is more complicated. More expanded matrix of indium selenide the most low frequency branch of impedance hodograph shows visualization of quantum capacitance  $C_Q$ , due as discretization of the energy spectrum InSe nanolayers [18] and finitude of tunneling times [19]. However, for the less expanded matrix has seen transition low branches hodograph in IV-“inductive” quadrant of the plane of complex impedance. The most interesting is that the observed phenomenon of “negative” capacitance in this case is not associated with the deformation  $\rho(\omega)$ , as it can see for GaSe <ODM>.

## CONCLUSIONS

1. X-ray diffraction analysis showed profound change in the structure of gallium selenide due to its intercalation by oligo-dimethylamino-methacrylate (ODM).
2. For GaSe <ODM> nanostructures obtained from the expanded in four times matrix, was shown reduction of loss tangent and dielectric constant and emergence high-frequency oscillations of the dielectric constant.
3. After the implementation oligomer in four times expanded GaSe matrix, correlation between the deformation of low-frequency branch real part of complex impedance and the phenomenon of transition related branches of the Nyquist diagrams in IV-“inductive” quadrant of the complex plane have been observed, but for the doubly expanded matrix of this correlation is absent.
4. Current-voltage characteristics of the GaSe <ODM> along to the crystallographic axis  $C$  have typical hysteresis for both degrees of splitting, but their appearance strongly depends on them.
5. Impedance hodographs represent lines almost parallel to the axis values of the imaginary part of complex impedance for nanostructures InSe <ODM>. The most low frequency branch of impedance hodograph shows visualization of quantum capacitance  $C_Q$ , due as discretization of the energy spectrum InSe nanolayers, and finitude of tunneling times with increasing the degree of expansion of the matrix indium selenide.

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