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Synthesis and Electrical Properties of Ag_8SnSe_6Argyrodite Thin Films

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The synthesis of Ag_8SnSe_6 argyrodite thin films with thickness 500 nm by selenization of Ag-Sn film at 480 °C was carried out. Thin films were investigated by X-ray diffraction. Ternary Ag_8SnSe_6 synthesized in orthorhombic structure with the lattice parameters $\boldsymbol{a}$ = 7.9081(6) Å, $\boldsymbol{b}$ = 7.8189(7) Å, $\boldsymbol{c}$ = 11.0464(9) Å, $\boldsymbol{V}$ = 683.03(10) Å^3. Resistive switching cell based on Ag_8SnSe_6 argyrodite with silver and graphite electrodes was fabricated. Electrical properties of cell were investigated using impedance spectroscopy and cyclic voltammetry. Cell structure and process in this cell were modeled by electric equvivalent circuit. Resistive switching phenomena in Ag/Ag_8SnSe_6/C cell at certain applied voltage were demonstrated.

Keywords: argyrodite, X-ray diffraction, electrochemical cell, impedance spectroscopy, cyclic voltammetry.

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Introduction

Resistive random-access memory (RRAM) develops intensively, which leads to the search and improvement of materials that can be used in elements of this memory. Interest to the practical application of RRAM caused by high speed read/write of information, high storage density and low power consumption, which making it one of the most promising [1, 2].

Resistive switching phenomenon caused by the migration of cations. As a result from these ions the channels of conductivity are created and destroyed. These processes occur in the electrochemical cell with solid electrolyte which is placed between the electrochemically active and inert electrodes [3]. As the solid electrolyte in these types of cells the metal chalcogenide with good conduction by Ag^+ or Cu^+ ions can be used. Among these compounds the Ag_2Se [4], Ag_2S [5], $Ge_{0,3}Se_{0,7}$ [6], $Ge_{0,2}S_{0,8}$ [7], Ag-Ge-Se [8] are extensively used. We know that Ag_8SnSe_6 argyrodite also has the resistive switching properties [9], so the study of the properties of thin films of this material is very important.

There are many methods for synthesis binary and ternary chalcogenide semiconductor thin films, one of the prospective methods is the process of selenization of precursors. The method is based on the temperature endurance of stoichiometric metal precursors in the vapor of elementary chalcogen (S, Se)[10-13].

These studies are a continuation of the work package aimed at studying the physical properties of Ag_8SnSe_6argyrodite [14-18]. The aim of this work is synthesis of argyrodite Ag_8SnSe_6thin films for further research and fabrication resistive switching cells that can potentially be used as the elements for a resistive memory.

I. Experimental

To synthesis of argyrodite thin films the selenization of Ag-Sn films was used, according to the stoichiometric ratio of these components in the ternary Ag_8SnSe_6 compound.

For the Ag-Sn thin films deposition process the target with a 40 mm diameter and a 3 mm thickness was fused. As the basic starting materials was used silver and tin of high purity (99.999%) in the following molar ratio of the component [Ag]/[Ag + Sn] = 0,85. The melting occured

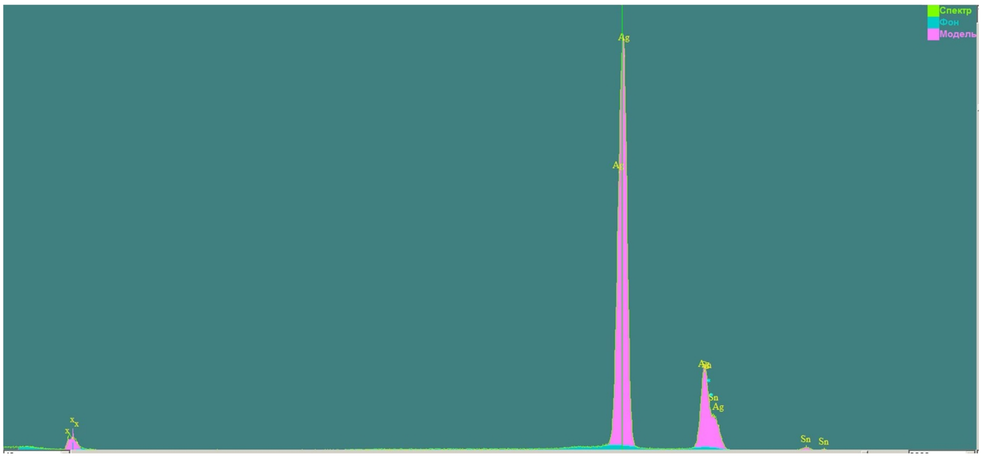

Fig. 1. Energy dispersive X-ray spectrum of Ag-Sn target.

according to the phase diagrams [19]. The elemental composition of the obtained target was investigated by energy dispersive X-ray analysis and presented in fig. 1. The spectrum shows that in the target, there are no impurities and that elemental composition of Ag-Sn corresponds to the necessary for the synthesis component ratio.

As the substrates was used the glass graphite, which is pre-cleaned in ultrasonic bath in distilled water and acetone during 30 minutes for each.

Deposition occurred using high-frequency magnetron sputtering method from the Ag-Sn target in an argon atmosphere. The distance between the substrates and the target was 60 mm, and the substrate temperature during deposition was T = 345 K. Deposition process lasted 30 minutes. The result was obtained Ag-Sn film 500 nm thickness.

Further obtained film was placed in a quartz ampoule with the elemental selenium of high purity (99.999%) and evacuated to a pressure of 10^{-6} Torr. Filled and evacuated ampoule was placed in a vertical furnace with two controlled zone for the synthesis of ternary argyrodite compounds.

Temperature synthesis of $Ag_8SnSe_6$was conducted according to the temperature dependence shown in fig. 2.

During synthesis process zone 1, where the substrates are located is slowly heated to 480° C with a speed of 100^o/h. When the desired temperature is reached the rapid heating of zone 2 with elemental selenium was starting to a temperature of 400 ^oC to form gaseous Se. In addition, between zones 1 and 2 created additional narrow area whose temperature was 700 ^oC, it was made to order the avoid the formation of gaseous selenium clusters that decrease the activity of its reaction with films Ag-Sn. When the required temperatures were reached the temperature exposure during 1 hour was performed and then rapidly cooled of zone 2 was started. The substrates cooling occurred with the same temperature dependence as heating.

Obtained thin films were investigated by X-ray diffractometer STOE STADI P [20] in a reflection mode with Cu $K\alpha_1$ radiation. Scanning was performed by points with recording step 2θ-0,015º, the exposure at the point - 300 s. The crystal structure determined by Rietveld method [21] in the software package FullProf.2k (version 5.60) [22, 23].

To investigate the electrical properties of the Ag_8SnSe_6 films and resistive switching phenomena the solid electrochemical cells based on argyrodite were created. Principle scheme of a cell with sandwich structure was shown in fig. 3.

Glass graphite substrate used as inert to silver ions Ag^+ electrode. Synthesized argyrodite was used as the solid electrolyte. To obtain active to silver ions Ag^+

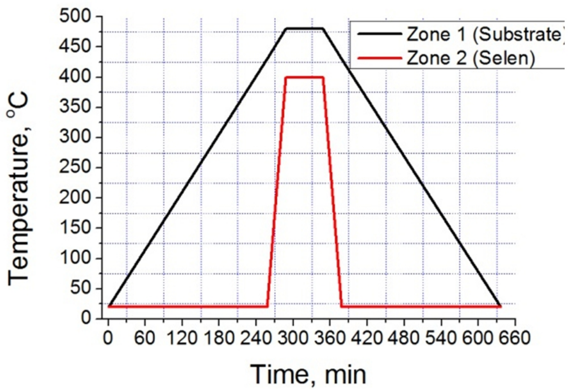

Fig. 2. Temperature profiles of Ag_8SnSe_6 synthesis by selenization method.

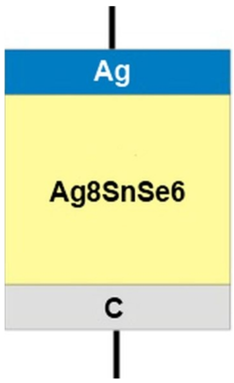

Fig. 3. Scheme of solid electrochemical cell $Ag/Ag_8SnSe_6/C$.

electrode magnetron sputtering of silver Ag on a thin film Ag_8SnSe_6 was performed. As the result resistive switching cell shown in fig. 4 was obtained.

The study of electrical parameters of the cell were performed using methods impedance spectroscopy in the frequency range 0.0001 Hz ÷ 1MHz and cyclic voltammetry using measuring complex “AUTOLAB PGSTAT100” by “ECO CHEMIE” (Netherlands), with software FRA-2 and GPES.

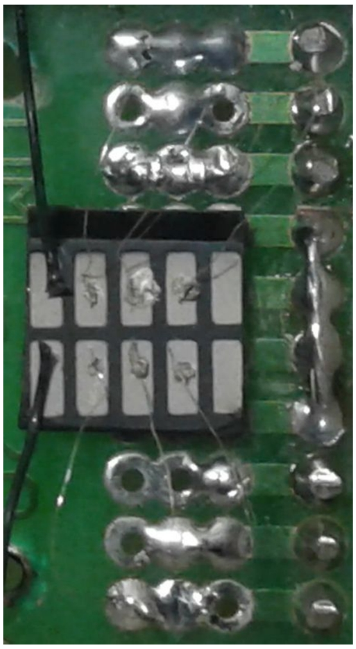

Fig. 4. $Ag/Ag_8SnSe_6/C$ resistive switching cell.

II. Results and discussion

Results of X-ray diffraction shown in fig. 5. On the spectrum observed peaks are related to the Ag_8SnSe_6 compounds. Crystal structure determination showed that the compound formed in orthorhombic phase with space group *Pmn*2$_1$. The crystal lattice parameters are a = 7.9081(6) Å, b = 7.8189(7) Å, c = 11.0464(9) Å, V = 683.03(10) $Å^3$. The results for the films in good agreement with the results for crystalline samples [24, 15, 17].

In fig. 6, 7 presented the results of impedance investigation of fabricated $Ag/Ag_8SnSe_6/C$ cell. On Nyquist plot there are two semicircles, one of which, such as high-frequency is very small (shown in inset). Presented diagram was modeled in the software package Zview2 using equivalent circuit (fig. 8).

Modeled equivalent circuit contains five series RC-elements, by which can describe the following processes in the cell and its structural components. The first element R1C1, which simulates high-frequency semicircle, corresponds to charge carriers present in the inert glass graphite electrode. The other four elements form the next big semicircle and are responsible for the following processes: R2C2 and R5C5 correspond to processes occurring at the border section silver and graphite electrode with a solid electrolyte. Element R3C3 modeling processes occurs in the solid electrolyte Ag_8SnSe_6, and R4C4 element responsible to the processes taking place on the grain boundaries in argyrodite thin film. Every single element through which current flows has individual resistance and capacitance parameters. Relevant parameters of each elements and correspond processes which they are modeling are presented in table 1.

To investigate the resistive switching phenomenon in the $Ag/Ag_8SnSe_6/C$ cell cyclic voltammetry method was used. The value of the applied voltage was located in the range ¬0,6 ¬ +0,6 V.

Resistive switching process happens by the mechanism presented in fig. 10 [25]. By applying to the $Ag/Ag_8SnSe_6/C$ cell an electrical voltage, and the positive pole attached to the silver electrode and

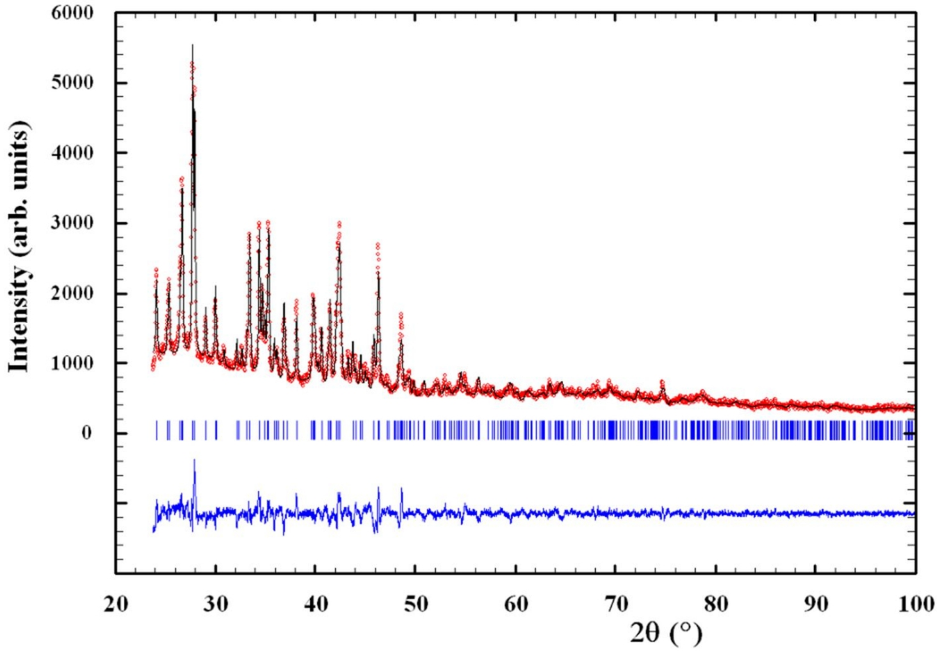

Fig. 5. X-ray diffractogram of synthesized Ag_8SnSe_6 argyrodite thin film.

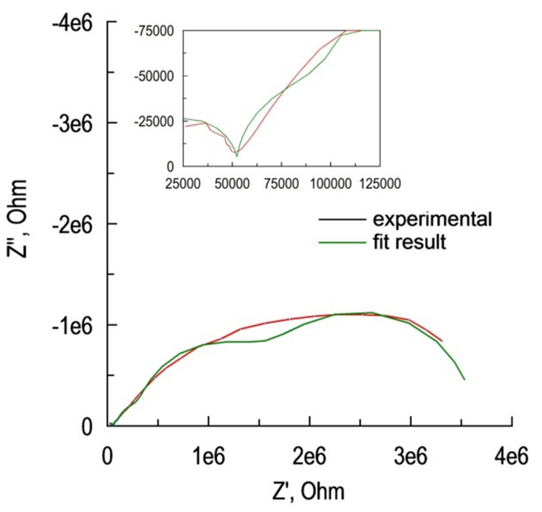

Fig. 6. Experimental and modeled Nyquist plot for the $Ag/Ag_8SnSe_6/C$ cell. On insert presented high-frequency part of plot. The values of real (Z') and imaginary (Z'') part of impedance given in Ohms.

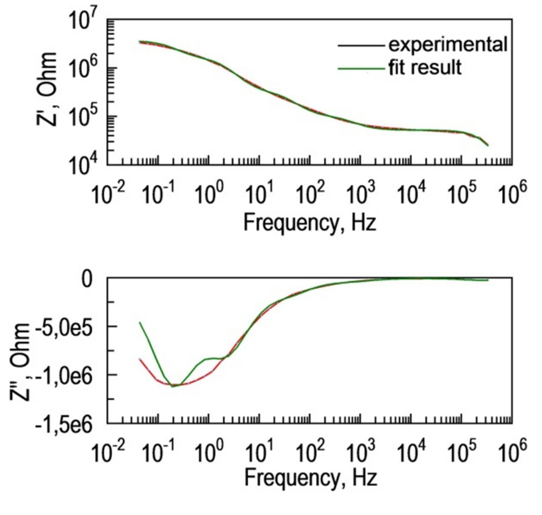

Fig. 7. Experimental and modeled Bode plot for the $Ag/Ag_8SnSe_6/C$ cell. The values of real (Z') and imaginary (Z'') part of impedance given in Ohms.

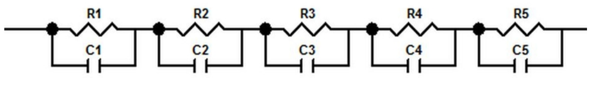

Fig. 8. Equivalent circuit of $Ag/Ag_8SnSe_6/C$ cell.

negativepole attached to graphite electrodes, located in the electrolyte silver Agatoms, oxidized to positively charged ions Ag^+ and there is a movement formed by ions to graphite electrode (fig. 10b).Since this electrode is blocking, the blocking and reducing of Ag^+ ions occurs and built, some kind of channel of conductance (fig. 10c). At the moment when it formed a sharp increase of current value or in other words the resistive switching are happens. By the change the polarity of the

Table 1

Element's parameters of equivalent circuit which used to modeling $Ag/Ag_8SnSe_6/C$ cell

	Parameters value	Error,%
R1	52,4 kΩ	1,42
C1	$9{,}45\cdot10^{-12}$ F	4,47
R2	2,04 MΩ	4,99
C2	$4{,}02\cdot10^{-7}$ F	10,56
R3	48,56 kΩ	9,46
C3	$4{,}87\cdot10^{-9}$ F	8,15
R4	214,1 kΩ	7,27
C4	$1{,}75\cdot10^{-8}$ F	7,91
R5	1,27 MΩ	5,33
C5	$5{,}13\cdot10^{-8}$ F	5,19

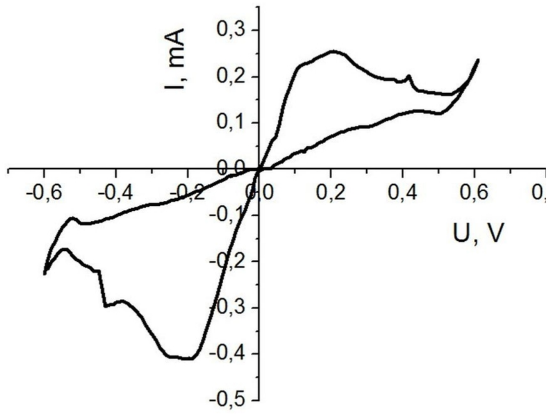

Fig. 9. Cyclic voltamperogram of $Ag/Ag_8SnSe_6/C$ cell.

electrodes occurs the reverse process, namely Ag^+ ions destroy the channel and move to volume of solid electrolyte (fig. 10d). By applying a voltage in the range 0,6V - + 0,6V, there is a 3 point of switch at 0.15, 0.42 and 0.6 V (fig. 9). In the experimental graph after these points the current decrease is observed, which is typical for bipolar resistive switching process during this phenomenon [26].

III. Conclusions

Was developed physical and chemical technology for synthesis Ag_8SnSe_6argyrodite thin films by magnetron sputtering of Ag-Sn films in appropriate stoichiometric ratios, and their subsequent temperature exposure in the vapor of elementary selenium at 480 °C. X-ray diffraction analysis confirmed the synthesis of ternary Ag_8SnSe_6 argyrodite compound in orthorhombic phase with space group *Pmn*2_1. Lattice parameters of thin films are a = 7.9081(6) Å, b = 7.8189(7) Å, c = 11.0464(9) Å, V = 683.03(10) $Å^3$ and are in good

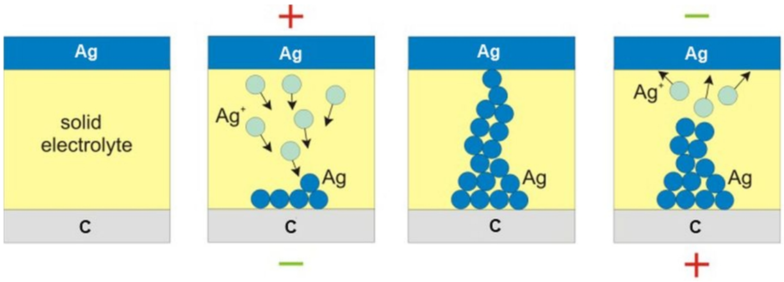

Fig. 10. Scheme of resistive switching process in solid state cells.

agreement with the parameters of polycrystalline samples.

Fabricated resistive switching cell based on the thin film of Ag_8SnSe_6 argyrodite with active to Ag^+ ions silver and blocking to them glass graphite electrodes.

Electrical investigation of the cell by impedance spectroscopy was carried out. This research allowed presenting the cell structure and processes that occur in cell using electrical equivalent circuit consisting of five RC elements each of which corresponds to a process in a cell and the resistance and capacitance parameters of each component are given.

Existence of resistive switching effect in $Ag/Ag_8SnSe_6/C$ thin film cells by measuring current-voltage characteristics (CVC) under normal conditions is presented. The study showed that at the applied voltage range 0 V –+ 0,6 V on the graph observed three resistive peaks at 0.15, 0.42 and 0.6 V. A similar result, but with different values of switching current observed with applying a voltage in the range from 0 V to ¬0.6 V.

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Синтез та електричні властивості тонких плівок аргіродиту Ag_8SnSe_6

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Проведено синтез тонких плівок аргіродиту Ag_8SnSe_6 товщиною 500 нм за допомогою температурної витримки плівок Ag-Sn в парах елементарного селену при температурі 480 °C. Проведено рентгеноструктурні дослідження отриманих плівок показали утворення потрійної сполуки Ag_8SnSe_6 у орторомбічній фазі з параметрами кристалічної гратки a = 7,9081(6) Å, b = 7,8189(7) Å, c = 11,0464(9) Å, V = 683,03(10) Å^3. Створено комірку резистивного перемикання на основі плівки Ag_8SnSe_6 з срібним та склографітовим електродами. Проведено дослідження електричних параметрів комірки методами імпедансної спектроскопії та циклічної вольтамперометрії. Ці дослідження дозволили змоделювати комірку та процеси, що в відбуваються за допомогою електричної еквівалентної схеми та показати наявність явища резистивного перемикання при певних прикладених напругах.

Ключові слова: аргіродит, рентгенівська дифрактометрія, електрохімічна комірка, імпедансна спектроскопія, резистивне перемикання.