# ABSTRACT

of the thesis
**"Promising methods for the synthesis and study of thin-film chalcogenide materials"**
for the Doctor of Philosophy (PhD) degree in the specialty "6D074000 – Nanomaterials and nanotechnology" of
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**Goal** of this thesis is to synthesize and study the structural, optical and electrical characteristics of thin films of antimony selenide chalcogenides and a copper-antimony-sulfur ternary compound.

**The tasks.** To achieve this goal, the following tasks were set:

− to develop a method for obtaining thin films of antimony selenide ($Sb_2Se_3$) and a ternary copper-antimony-sulfur compound ($Cu_xSb_yS_z$)

− to study the phase composition formation mechanism in Cu-Sb-S systems in the process of magnetron sputtering of antimony-copper metal precursors with further sulfurization;

− to carry out compositional, morphological and structural analysis, phase identification, as well as to study the optical and electrical properties of antimony selenide and copper-antimony-sulfur ternary compounds.

**Research methods**. The following methods were used to implement the tasks set: X-ray phase analysis and Raman spectroscopy, scanning electron microscopy, photoluminescent spectroscopy, optical absorption/transmission spectroscopy, four-probe method for measuring resistivity, and the Hall effect.

**The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense:**

1. Correction of the Cu:Sb ratio within 1.77–1.88 in precursors obtained by magnetron sputtering and their subsequent sulfurization at temperatures of 140°C and 180°C leads to the formation of ternary phases $Cu_{12}Sb_4S_{13}$ and $Cu_3SbS_4$.

2. The appearance of a characteristic peak near 250 $cm^{-1}$ in the Raman scattering spectra of $Sb_2Se_3$ films is due to local oxidation of antimony during spectrum recording due to the increased power density of the laser used.

3. The charge carriers transport in $Sb_2Se_3$ films in the low-temperature regime is carried out by means of the hopping mechanism of conduction, which is characterized by an activation energy of ~25 meV.

**Rationale for the need for research work.** An urgent issue in the field of highly efficient nano- and microsized semiconductor optoelectronic devices is the search for new materials that reduce the cost and increase the functionality of technological solutions. Recently, compounds based on chalcogenides of antimony selenide and ternary compounds of copper-antimony-sulfur have attracted more and more interest among scientists. These materials are used in various branches of optoelectronics due to their structural, optical and electronic properties. Despite the availability of various methods for the synthesis of films of antimony selenide and copper-antimony sulfide, including deposition from a liquid phase, most of them

have disadvantages, which manifest themselves in the low quality of the initial films. Vacuum thermal deposition is one of the methods to obtain a high-quality structure with desired semiconductor properties. This method is based on the evaporation of powders of initial chemical elements or their compounds at temperatures of 500-600 °C. However, to meet the requirements not only for the quality of thin films, but also for their industrial adaptation, it is advisable to use widely available technologies that allow production on an industrial scale. Magnetron sputtering and chemical vapor deposition are among the common and frequently used industrial methods for the synthesis of thin-film materials.

The quality of thin films of chalcogenide materials is confirmed by studying their phase structure. In this case, it is especially important to use non-invasive methods that do not cause changes in the internal structure of the samples during the experiment. One of the promising methods of non-invasive structural analysis is Raman spectroscopy. Its application makes it possible to obtain information on the surface phases of films quickly and without additional operations for sample preparation. One of the little-studied and topical problems of Raman spectroscopy as applied to thin films of antimony selenide is the correct interpretation of certain vibrational modes. In addition, the crystalline properties of the resulting material affect the electrical properties. Measurements of the Hall effect and resistivity as a function of temperature provide valuable information on the mechanisms of conduction and parameters such as charge carrier density, mobility, and ionization energy of small defects. Studies of the electrical conductivity and defects of these compounds also remain relevant today.

Thus, the possibility of synthesizing thin films of chalcogenide materials by widely available methods is important for practical applications. A promising approach in this direction is the development of methods of magnetron sputtering and chemical vapor deposition, which do not require large energy inputs and make it possible to control the synthesis process to obtain materials with desired properties. In addition, of great interest, from a scientific point of view, is the identification of vibrational modes of molecules of chalcogenide materials and studies aimed at studying the electrical properties for subsequent analysis of the synthesized films.

**Description of the main results of the study.**

This thesis presents methods developed in the course of research for the synthesis of promising thin-film materials based on antimony selenide and ternary compounds of copper-antimony-sulfur for semiconductor optoelectronics, as well as the results of a study of their structural and optical properties. These compounds have the potential to be used in solar cells due to the relative simplicity and low temperature of their preparation, the availability of starting materials in nature, and favorable optical properties.

A two-stage method for the selective synthesis of a thin film of $Cu_{12}Sb_4S_{14}$ and $Cu_3SbS_4$ by changing the area of precursors and the sulfurization process is presented. Metal precursors were simultaneously deposited by RF magnetron sputtering using a target consisting of Cu segments and a Sb base. By controlling the evaporation temperature of sulfur during the sulfurization/annealing process, two different crystalline phases were obtained. The identification of crystalline phases was carried out using the methods of X-ray diffraction and Raman scattering. At a sulfur evaporation temperature of 140 °C, the precipitated crystalline phase is tetrahedrite $Cu_{12}Sb_4S_{14}$ with a cubic structure. During the evaporation of sulfur at a temperature of 180 °C, the main phase is famatinite $Cu_3SbS_4$ with a tetragonal structure. Optical analysis made it possible to estimate the band gap energies, which were 1.47 eV and 0.89 eV for $Cu_{12}Sb_4S_{14}$ and $Cu_3SbS_4$, respectively. In this case, both phases are characterized by direct allowed transitions. The PL measurement shows a broad peak centered around 0.83 eV for a sample prepared at 180°C. For the sample synthesized at 140°C, no PL signal was detected.

In addition, it was shown that the process of high-frequency magnetron sputtering followed by selenization is suitable for growing $Sb_2Se_3$ films with a high-quality crystal structure and optoelectronic properties. The grain sizes of selenium-antimony precursor films do not exceed 80 nm. Some compositional and morphological differences are observed when comparing films grown on glass, glass/Mo, and Si substrates. Samples on silicon have compositions close to stoichiometric and more regular grains with increasing selenization temperature. As expected, with an increase in the selenization temperature, a general increase in the grain size is observed for all substrates. The area of most small grains remains in the nanometer range. The results of X-ray spectroscopy show that no columnar orientation is observed with this growth method. The Raman scattering method revealed the localized presence of rhombohedral and amorphous Se, which is consistent with the EMF measurements and indicates Se condensation during cooling after the selenization process. Optical measurements carried out on samples with Si substrates made it possible to determine the band gap with a direct optical transition close to 1.06 eV for the used selenization temperatures. Photoluminescence performed on the same samples demonstrates a dominant broad band at ~0.85 eV for the samples selenized at 300°C and 350°C, and a sharper and more intense peak close to 0.75 eV for the sample selenized at 400°C. An intense peak with an energy close to the band gap is an important feature of materials for solar cell applications. However, the electrical characteristics of samples grown on glass substrates exhibit relatively low concentrations of free holes and low mobility. The study shows that in the low-temperature regime, electron transport occurs due to jumps over the nearest neighbors.

In the framework of this work, the peak at 250 $cm^{-1}$ was identified in the obtained $Sb_2Se_3$ samples. It was found that the peak belongs to the antimony oxide phase, which occurs due to oxidation when using a high-density laser. Spectrum acquisition regimes are established for antimony selenide samples to avoid Se evaporation, where the main requirement is a low laser power density ~ 170 $MW/m^{-2}$. In addition, it was found that Raman spectroscopic measurements with a high laser power should be carried out with these samples in vacuum in order to avoid oxidation. One of the important results of the work is the observation and determination of the stability limits of the $Sb_2Se_3$ compound: high-energy conditions, such as increased power of the exciting laser or sample temperature, easily lead to the formation of the $Sb_2O_3$ phase, so this fact must be taken into account in the synthesis of compounds.

In addition to the RF magnetron sputtering method, $Sb_2Se_3$ samples were synthesized by two simple and inexpensive methods of electrochemical deposition and metal precursor selenization. Films with thicknesses of 60–300 nm were studied. For an electrodeposited sample annealed at 270°C, the effective optical band gap of 1.27 eV was determined using the sigmoidal absorption approximation. In this case, for a sample selenized at 350 °C, based on the analysis of the Tauk plot, the band gap was determined to be 1.12 eV with a direct optical transition. In the film selenized at 350°C, the presence of the cubic $Sb_2O_3$ phase was detected, which is associated with the precipitation inside the reactor during cooling of unreacted antimony particles, which, upon contact with air, can react with oxygen faster than with selenium. X-ray diffraction analysis demonstrates the predominant growth of crystallites in the vertical direction in the sample selenized already at 270°C. Thus, the results of X-ray diffraction indicate the possibility of preferred growth modifications in certain directions, which depend on the growth method and annealing temperature.

**Substantiation of the novelty and importance of the obtained results.**

1. The conditions for the formation of ternary phases $Cu_{12}Sb_4S_{13}$ and $Cu_3SbS_4$ were studied for the first-time during synthesis by the method of RF magnetron sputtering of metal precursors followed by sulfurization at temperatures of 140 °C and 180 °C;

2. For the first time, for antimony selenide films, a hopping mechanism of charge transfer at low temperatures due to jump-like displacements of electrons over the nearest neighboring acceptor levels, characterized by an activation energy of ~25 meV, was proposed;

3. A new interpretation is proposed for the appearance of a peak at 250 $cm^{-1}$ in the Raman scattering spectra of antimony selenide films, which is a consequence of local oxidation of antimony under the action of a laser with an increased power density.

**Compliance with the directions of development of science or government programs.** All studies presented in this dissertation were carried out within the framework of the following programs and projects: the target funding program of the Ministry of Foreign Affairs of the Republic of Kazakhstan IRN BR05236404 (2018-2020), projects UID/CTM/50025/2019 and RECI/FIS-NAN/0183/2012 (FCOMP -01-0124-FEDER-027494) within the framework of the COMPETE 2020 Program of the Portuguese Science and Technology Foundation, project IF/00133/2015, grant funding project of the Ministry of Education and Science of the Republic of Kazakhstan AP05133651 (2018-2020), Erasmus 2016/17 program.

**The author's personal contribution** consists in setting up and conducting experiments, summarizing and interpreting the results obtained, and writing articles.

**Abstracts.** The materials of the dissertation work were reported and discussed at various international, republican conferences and symposiums:

1. 43rd International Conference on Micro and Nanoengineering (Braga, Portugal, September 18-22, 2017);

2. Conference of students and young scientists Satpayev readings on the topic "Scientific heritage of Shahmardan Yessenov" (Almaty, 2017);

3. 2018 MRS Spring Meeting, Symposium EN19. Novel Inorganic Semiconductor for Optoelectronics and Solar Energy (Phoenix, Arizona, USA, April 2-6, 2018);

4. International scientific conference of students and young scientists, "Farabi Alemi" (Almaty, April 9-12, 2018);

5. 2018 Spring Meeting (Strasbourg, France, June 18-22, 2018);

6. International Conference on Materials Research and Nanotechnology (Rome, Italy, June 10-12, 2019).

**Publications.** The results of the work performed are reflected in 6 scientific papers, including:

Scientific articles indexed by the Scopus and WoS database:

1. **A. Shongalova**, M.R. Correia, B. Vermang, J.M.V. Cunha, P.M.P. Salomé and P.A. Fernandes, On the identification of $Sb_2Se_3$ using Raman scattering //MRS communications. – 2018. – Т. 8. – №. 3. – С. 865-870. doi:10.1557/mrc.2018.94. *(quartile Q3, percentile General material science – 62, IF=1.9);*

2. **Shongalova A.**, Correia M. R., Teixeira J. P., Leitão, J. P., González J. C., Ranjbar S, S. Garud, B. Vermang, J.M.V. Cunha, P.M.P. Salomé, Fernandes, P. A. Growth of $Sb_2Se_3$ thin films by selenization of RF sputtered binary precursors //Solar Energy Materials and Solar Cells. – 2018. – Т. 187. – С. 219-226. doi: 10.1016/j.solmat.2018.08.003 (*quartile Q1, percentile Material scince: Electronic, Optical and Magnetic materials– 92, IF=6.01*);

3. Fernandes, P. A., **Shongalova, A.,** da Cunha, A. F., Teixeira, J. P., Leitão, J. P., Cunha, J. M. V., ... & Correia, M. R. Phase selective growth of $Cu_{12}Sb_4S_{13}$ and $Cu_3SbS_4$ thin films by chalcogenization of simultaneous sputtered metal precursors //Journal of Alloys and Compounds. – 2019. – Т. 797. – С. 1359-1366. doi: 10.1016/j.jallcom.2019.05.149 (*quartile Q1, percentile Mechanical engineering – 93, , IF=6.9*);

4. N Cifuentes, S Ghosh, **A Shongalova**, MR Correia, PMP Salome, PA Fernandes, S Ranjbar, S Garud, B Vermang, GM Ribeiro, JC Gonzalez, Electronic conduction mechanisms and defects in polycrystalline antimony selenide //The Journal of Physical Chemistry C. – 2020. – Т. 124. – №. 14. – С. 7677-7682. doi: 10.1021/acs.jpcc.0c00398 (*quartile Q2, percentile Physical and theoretical chemistry – 81, IF=4.1)*

Scientific article published within the framework of the international conference:

5. A Shongalova, M Aitzhanov, S Zhantuarov, K Urazov, P Fernandes, N. Tokmoldin, M.R. Correia, Shongalova A. et al. Comparison of antimony selenide thin films obtained by electrochemical deposition and selenization of a metal precursor //Materials Today: Proceedings. - 2020. - Т. 25. - S. 77-82. doi: 10.1016/j.matpr.2019.11.291 (*General Materials Science category - 38*)

Scientific article in publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Education and Science of the Republic of Kazakhstan:

6. A Shongalova, D Muratov, B Rakhmetov, K Aimaganbetov, S Zhantuarov, Shongalova A. et al. On thermal stability of antimony thin films for solar cells applications // Bulletin. Series Physical (VKF). - 2019. - T. 68. - No. 1. - S. 47-51. doi:10.26577/rcph-2019-1-1093