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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

ELECTRON AND PHONON PROCESSES IN THIN FILMS OF PbS(Se) OBTAINED BY CHEMICAL BATH DEPOSITION

Speciality: 2220.01 – Semiconductor Physics

Field of science: Physics

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GENERAL DESCRIPTION OF WORK

The actuality of the subject and degree of elaboration: Recently, there has been an intense interest in obtaining and researching new nanostructured semiconductor functional materials based on lead chalcogenides. The main reason for this is that lead chalcogenides obtained by various innovative methods have nonlinear optical properties, selective and passive fiber transmission properties for chemical sensors, and high photosensitivity in the infrared (IR) region of the spectrum.

The rapid development of infrared technology is closely related to the improvement of the synthesis and acquisition technology of semiconductor materials sensitive to this region of the spectrum. Therefore, functional semiconductor compounds and their thin films are of special importance in the preparation of various devices due to their electronic and optical properties. The wide application of thin films and nanostructures in IR techniques has recently increased the attention to scientific research in this field, the acquisition of new semiconductor thin films sensitive to the IR region of the spectrum, and the study of their structural and physical properties have become one of the most urgent issues of semiconductor physics. The narrowband semiconductors belonging to A^4B^6 group are the most valuable materials for IR optics. This is mainly due to the fact that the converters made on the basis of those materials are multifunctional. As a result of the application of high-tech methods, the increase in interest in the creation of quantum dots, quantum wires and other low-dimensional objects from the mentioned materials is also related to their application in opto- and nanoelectronic devices and alternative energy systems. At the modern stage of physics and technology of semiconductors, special attention is paid to the change of physical properties depending on the dimensions when passing from polycrystalline structures to nanostructures. One of the reasons for the growing interest in nanostructured lead chalcogenides is their flexible, compact, and low power consumption operating in the IR region. Materials related to the study of the optical properties of narrowband semiconductors with quantum dots are widely analyzed in the

scientific literature. Studies show that the study of nonlinear optical properties in the IR region of the spectrum is important to know the presence and properties of quantum dots in these semiconductors. It was found that PbS, PbSe, $PbSe_xS_{1-x}$, which are narrowband semiconductors belonging to the IV-VI group, have nonlinear optical properties and two-photon absorption properties in the near and mid-IR region of the spectrum and can be successfully applied in low-cost optical devices. The analysis of the results of such studies shows that the synthesis of lead chalcogenides containing nanorods, the study of optical and structural properties is of scientific and practical relevance. It was determined that the type of conductivity in the samples changes depending on the thickness. Among semiconductor materials, metal sulfides and solid solutions based on them are in high demand due to their multifunctional properties. Despite the fact that photoreceptors made on the basis of lead sulphide have been known for more than 50 years, they are still relevant today. The study of the literature shows that the combined light scattering method is widely used to identify the volume and structure of nanostructured materials obtained on the basis of Pb(S, Se, Te) systems and to determine the scattering mechanisms.

Narrow-band lead chalcogenides (PbX, X=S, Se, Te) are among the most studied compounds in recent years due to their wide application and interesting physical properties. The thin films of these compounds are of great interest due to their use in the preparation of IR detectors, gas sensors, photodiodes, solar cells, IR lasers, and thermoelectric converters[1].

In recent years, scientific research devoted to the structure and optical properties of narrow bandgap semiconductors with colloidal quantum dots has been intensively increasing.

The increasing functional demands on lasers based on solid materials have led to extensive research into the optical properties of narrow-bandgap semiconductors with two-photon absorption

[1] Маскаева, Л.Н. Технология тонких пленок и покрытий / Л.Н.Маскаева, Е.А.Федорова, В.Ф.Марков. учебное пособие, –2019, –236 с.

characteristics[2]. From the conducted studies, it is concluded that it is possible to adjust the optoelectronic properties of lead chalcogenides (PbSe and PbS) by thermal processing, by changing the relative concentration of the chalcogen components included in the composition, as well as by changing the diametrical sizes of the controllable quantum dots (in the range of 8.1÷16.1 nm)[3]. Other studies of this kind show that the control of nanoparticle sizes in the ranges of 1.32 ÷ 2.26 nm and 1.28–2.48 nm in PbS(PbSe) materials obtained by the hot injection method, depending on the technological mode, lays the foundation for purposeful control of structure, optical and electrical properties[4].

Due to the large boron radius of the exciton (8 nm), it is possible to experimentally observe quantum size effects to a noticeable extent in nanoparticles of compounds based on lead chalcogenides[5].

In most cases, the authors attribute the more intense bands observed during combined light scattering to transverse (TO) and longitudinal (LO) phonons. In order to minimize photooxidation processes in lead chalcogenides, it is necessary to conduct optical studies with low excitation intensity. The mentioned analyzes show that the correct identification of the results requires the availability of additional complex data. Thus, the goal set in the dissertation and the research conducted are quite relevant.

The object and subject of the research:

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[2] Wawrzynczyk, D. Third-order nonlinear optical properties of infrared emitting PbS and PbSe quantum dots / D.Wawrzynczyk, J.Szeremeta, M.Samoc et al. // The Journal of Physical Chemistry C., –2016. –T.120, № 38, –p.21939-21945.

[3] Liu, J. Precipitation and optical properties of PbSexS1-x quantum dots in glasses / J.Liu, J.Liu, W. Zhang et al. // Journal of Non-Crystalline Solids, –2023. –T. 604, –p.122156-122160.

[4] El-Menyawy, E.M. Structural, optical and electrical properties of PbS and PbSe quantum dot thin films / E.M.El-Menyawy, G.M.Mahmoud, R.S. Ibrahim et al. // Journal of Materials Science: Materials in Electronics, –2016, –T.27., –p. 10070-10077.

[5] Мараева, Е.В. Получение и исследование наноструктурированных поликристаллических слоев и систем с квантовыми точками на основе халькогенидов свинца / Е.В. Мараева // Фундаментальные проблемы радиоэлектронного приборостроения, –2014. –Т. 14, № 3, –с. 47-50.

The object of the research is PbS, PbSe, $PbS_{0,5}Se_{0,5}$ thin films obtained by chemical bath deposition in triethanolamine component (and triethanolamine-free) medium at room temperature and their powder samples, and the subject is the study of electronic and phonon processes in the obtained substances.

Purposes and tasks of research:

To obtain PbS(Se), $PbS_{0.5}Se_{0.5}$ nanostructured thin films and powders at different temperatures by chemical bath deposition method, to determine the regularities of changes in electronic properties depending on the structure and the possibilities of application in infrared technology.

To achieve the goal, the following issues were resolved:

- PbSe thin film and powder were obtained by chemical bath deposition at 60 °C and room temperatures, the effect of the triethanolamine component on the course of the reaction was determined;
- PbS thin film and powder were obtained at 40°C and room temperature;
- Thin films and powder of $PbS_{0.5}Se_{0.5}$ were obtained at room temperature and 50°C;
- X-ray spectra and Raman spectra of PbS, PbSe, $PbS_{0.5}Se_{0.5}$ thin films and powders obtained at different temperatures were recorded;
- The surface morphology of PbSe and $PbS_{0,5}Se_{0,5}$ thin films and powders was studied in the scanning atomic force microscope;
- Temperature dependence of electrical conductivity of PbS, PbSe and $PbS_{0,5}Se_{0,5}$ thin films was studied;
- The optical parameters of PbSe and $PbS_{0,5}Se_{0,5}$ thin films were studied by the Ellipsometry method and the results were analyzed using the "Graphycal analysis" program;
- The optical absorption coefficient of PbS, PbSe and $PbS_{0,5}Se_{0,5}$ thin films in the infrared region of the spectrum was measured;
- The optimal sizes of nanoparticles have been determined through X-ray diffraction scattering, and their effects on Raman scattering have been analyzed;
- Thermogravimetric analysis of PbS, PbSe and $PbS_{0,5}Se_{0,5}$

powders in the temperature range of 20-800°C was carried out.

Research methods:

X-ray diffraction, Raman spectroscopy, optical spectroscopy, and differential scanning calorimetry (DSC) methods were applied in the conducted researches for ellipsometric measurements, nanostructure, phonon spectrum and electronic properties of PbS, PbSe and $PbS_{0,5}Se_{0,5}$ substances.

The main provisions submitted to the defense:

1. Development and synthesis of the technology for obtaining thin layers of lead chalcogenides (PbS, PbSe and $PbS_{0,5}Se_{0,5}$) by chemical bath deposition at different temperatures;

2. With the increasing amount of the triethanolamine component in the mixed solution during the synthesis, shifting band gap of the PbS thin film toward lower energies and reacing its maximum value in the absence of triethanolamine;

3. In the PbSe powder obtained without adding the triethanolamine component to the solution, and with the addition of triethanolamine, observation of nanorods with a widths of 376 nm and150 nm, a lengths of 3-4 μm and 5-6 μm, respectively;

4. The best-fit case for the spectral dependencies of the real and imaginary parts of the dielectric function of the nanostructured PbSe thin film corresponds to a 2D-type critical point;

5. The value E=2.5 eV found for the PbSe thin film is close to the theoretically calculated value of E=2.3 eV and matches the two-dimensional (2D) critical point (m=0) and the $L_4 \rightarrow L_6$ transition;

6. Relation of peaks observed in Raman scattering spectra observed in PbS, PbSe and PbS0.5Se0.5 samples to both transverse and longitudinal optical phonons;

7. In the emission spectra of PbS, PbSe, and $PbS_{0.5}Se_{0.5}$ samples, the peaks observed at various frequencies in the infrared region were identified with their corresponding functional groups, and the band gap width was found to vary between 0.35 eV ÷ 0.39 eV;

Scientific novelty of the study:

1. A technology has been developed for producing thin films and powders of lead chalcogenides (PbS, PbSe and $PbS_{0,5}Se_{0,5}$) in a mixed solution with chemical bath deposition at various temperatures and thin

films and fine powders with a thickness of ≈200 nm have been obtained.

2. Nanorods with a width of 376 nm and a length of 3-4 μm were observed in the PbSe powder obtained without adding the triethanolamine component to the solution, and when the same component was added, nanorods with a length of 5-6 μm and a width of 150 nm were observed.

3. The results of ellipsometric measurements for PbS, PbSe, and $PbS_{0.5}Se_{0.5}$ thin films were analyzed using the "Graphical Analysis" program. It was found that the value E=2.5 eV for PbSe is close to the theoretically calculated value of E=2.3 eV, corresponding to the two-dimensional (2D) state (m=0) and the Brillouin zone $L_4 \rightarrow L_6$ transition. For $PbS_{0.5}Se_{0.5}$, the value E=3.5 eV corresponds $L_5 \rightarrow L_6$ transitions.

4. In the X-ray diffraction spectra, the 2θ angles for PbSe and $PbS_{0.5}Se_{0.5}$ coincide with each other, while for PbS, these angles shift towards smaller values. The difference between the angles of the peaks corresponding to the (111) planes for $PbS_{0.5}Se_{0.5}$ and PbS is approximately $2\theta \approx 0.9^{\circ}$. However, as the angles increase, this difference gradually increases, reaching $2\theta \approx 3^{\circ}$ for the peaks corresponding to the (422) planes.

5. As a result of half-substitution of selenium with sulfur, the shift of the peaks observed in the Raman scattering spectrum towards relatively high frequencies (70 cm^{-1}) is shown to be related to the increase in the crystallite size of the nanoparticles, which gives rise to scattering on the (111) plane. In the scientific literature, the maximum observed in the spectrum of the scattering frequency ~ 254 cm^{-1} is related to scattering from vibrations of Se_8 rings, and the peaks observed at frequencies 120÷122 cm^{-1} are related to scattering from both transverse and longitudinal phonons.

6. In the samples of PbS, PbSe and $PbS_{0,5}Se_{0,5}$, the functional groups to which the peaks corresponding to different frequencies observed in the infrared region of the spectrum belong were found, and the values of the width of the band gap for those layers are determined to be between 0.3÷0.39eV and their compatibility with the values indicated in the literature is determined. As the amount of triethanolamine in the mixed solution increases, the band gap of the obtained PbS thin film shifts to lower energies, and this quantity takes its maximum value in the

absence of triethanolamine.

Theoretical and practical significance of the study:

The analysis of the optical absorption spectra of PbS, PbSe and $PbS_{0,5}Se_{0,5}$ thin films obtained by the chemical bath deposition method in the presented dissertation shows that their fundamental optical absorption edge, including the width of the optical band gaps, changes in the range of Eg~0.347÷0.392 eV and falls into the infrared region of the spectrum. These results show that the studied samples are narrowband semiconductors, and have promising applications in infrared detectors, along with a simple acquisition technology. The conducted researches show that it is possible to obtain active operating elements of optical converters and sensors with the required non-linear optical properties, ion selective sensor properties by purposefully controlling the effective sizes of PbS, PbSe and $PbS_{0,5}Se_{0,5}$ nanoparticles obtained by the mentioned method. PbS, PbSe and $PbS_{0,5}Se_{0,5}$ nanoparticle thin films obtained by chemical bath deposition can be used in passive fiber transmitters because they have a relatively weak absorption coefficient in the mid-infrared region of the spectrum.

Approbation and application:

The results of the dissertation were presented at the following scientific conferences:

- The 15th International Conference on 'Technical and Physical Problems of Electrical Engineering' (ICTPE) (Istanbul, 2019)
- The 16th International Conference on 'Technical and Physical Problems of Electrical Engineering' (ICTPE) (Istanbul, 2020);
- The 19th International Conference on 'Technical and Physical Problems of Electrical Engineering' (ICTPE) (Istanbul, 2023);
- The 20th International Conference on 'Technical and Physical Problems of Electrical Engineering' (ICTPE) (Istanbul, 2024);
- İnternetional Conference Advanced Laser Technologies, (ALT24), September 2024, Vladivostok, Russia ;
- Naxçıvan Muxtar Respublikasının 100 illiyi və Azərbaycan Respublikası Elm və Təhsil Nazirliyi Fizika İnstitutu alimlərinin yubileyinə həsr olunmuş beynəlxalq konfrans (2024), Naxçıvan ;

15 scientific works have been published in local and foreign scientific publications on the subject of the dissertation work. 9 of them

are articles and 5 are international conference materials.

The name of the organization where the dissertation work is done: The dissertation work was performed at the Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan and the Institute of Natural Resources of the Ministry of Science and Education of the Republic of Azerbaijan.

The structure and volume of the dissertation: Dissertation work is explained in 132 pages, consisting of an introduction, 5 chapters, conclusions and a bibliographic list of 124 cited literature.

There are 59 pictures and 7 tables in the thesis work. Introduction – 24204 marks, Chapter I – 48381 marks, Chapter II – 30235 marks, Chapter III – 22870 marks, Chapter IV – 9608 marks, Chapter V – 23859, Conclusion – 3742 marks.

The total volume of the dissertation consists of 162899 characters, excluding tables, pictures, and bibliography.

THE MAIN CONTENT OF THE DISSERTATION

In the introduction, the relevance of the dissertation topic is established, the purpose, scientific novelty, and practical importance of the work are outlined, the main propositions submitted for defense are presented, the degree of approval and publications are reported, and a brief overview of the main content of the chapters is provided.

The first chapter examines the literature review on the study of PbS, PbSe and $PbS_{0,5}Se_{0.5}$ thin films. PbS, PbSe and $PbS_{0,5}Se_{0.5}$ thin films and powders obtained by chemical bath deposition were comparatively analyzed on the basis of information obtained from literature materials on their wide range of technical applications, structure, physical properties. It has been widely discussed that the chemical bath deposition method is a more qualitative and convenient method in terms of application. From the study of literature materials, it is possible to come to the conclusion that PbX(S,Se,Te) semiconductor thin films obtained by chemical bath deposition are more widely used in electrical technology. It is noted that the optical properties of PbSe and $PbS_{0,5}Se_{0.5}$ semiconducting thin films have not been studied properly. From the literature, it can be concluded that transverse and surface phonon modes

are usually not observed in Raman measurements due to symmetry constraints. Such studies show that surface layers and layer defects in PbS, PbSe, $PbS_{0,5}Se_{0.5}$ thin films play an important role in controlling physical parameters. It is also known from the literature that quantum confinement effects of PbS, PbSe and $PbS_{0,5}Se_{0.5}$ thin films seriously affect the dielectric function of low-size semiconductors.

Thus, the extensive analysis of the scientific literature shows that the research carried out in the dissertation work will contribute to the solution of the important problem, both scientifically and practically.

In the second chapter, the technology of obtaining PbS, PbSe, $PbS_{0,5}Se_{0.5}$, the advantages of this method are briefly discussed with reference to literature materials. Then the results about the technology of obtaining thin films of the materials (PbS, PbSe, $PbS_{0,5}Se_{0.5}$) used in the dissertation work are interpreted. The properties of PbS thin film and powder obtained by chemical bath deposition at 40°C were investigated based on the amount of triethanolamine component. The yield of PbS compound was determined based on the lead acetate component in the solution.

The solution used for obtaining a PbS thin film by chemical bath deposition is prepared by taking the same amount (by volume) of each of the solutions prepared in the following manner: lead acetate $Pb(CH_3COO)_2$ - 0.07 M; sodium hydroxide (NaOH)-0.3 M; triethanolamine $N(CH_2CH_2OH)_3$ - 0.06 M; Thiourea $(NH_2)_2CS$ -0.17 M. The chemical bath deposition process was carried out in a 60 ml laboratory beaker at 40^0C[6]. Also, by taking the same amount of these solutions at room temperature, PbS thin film and powder were obtained at room temperature.

To clarify how the amount of triethanolamine in the solution affects the properties of the resulting PbS thin film, three different examples were prepared:

N: Thin film obtained from a 0.06 M triethanolamine solution.

T4: Thin film obtained from a 0.24 M triethanolamine solution,

[6] Hüseynəliyev, M.H. /Kimyəvi çökdürmə yolu ilə alınmış PbS nazik təbəqələrinin optik xassələrinə trietanolamin komponentinin təsiri / M.H.Hüseynəliyev, S.N.Yasinova, L.N. İbrahimova // AMEA Naxçıvan Bölməsi, "Xəbərlər", 2018, №2, s.254-258.

which is four times more concentrated.

T0: Thin film obtained from a mixed solution without the presence of triethanolamine.

In all three cases, brown PbS thin films with good adhesion and homogeneity were obtained on glass.

The solution used for obtaining a thin film of PbSe by chemical bath deposition at a temperature of 60°C is prepared by taking the same amount (by volume) from each of the solutions prepared in the following manner: lead acetate $Pb(CH_3COO)_2$ - 0.07 M; sodium hydroxide (NaOH)-0.3 M; triethanolamine $N(CH_2CH_2OH)_3$ -0.06 M; sodium selenosulfate Na_2SSeO_3 -0.17 M. The sodium selenosulfate solution used to enter the selenium component into the solution was obtained by boiling 0.425 g of metallic selenium powder and 1.245 g of sodium sulfide in 100 ml of distilled water at a temperature of 90^0C for 7 hours in a arefrigerator[7].

After this process, a thin layer of PbSe with a thickness of 183.41 nm is obtained on the glass substrate and on the walls of the used laboratory beaker[8].

Also, PbSe thin film and powder were obtained by adding the same amount of these solutions at room temperature. As a result, a 239.36 nm thick PbSe thin film was obtained on glass.

The thermodynamic parameters of the reaction were calculated based on the final equation of the reaction carried out using the values of thermodynamic parameters such as enthalpy and entropy of formation and Gibbs energy taken from literature materials corresponding to PbSe powder. The chemical and mineralogical composition of PbSe powder was shown, and lead was also determined by the iodometric method.

Chemical bath deposition is considered to be the most commonly used and controllable method. Therefore, this method is

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[7] Luther, J.M. Schottky solar cells based on colloidal nanocrystal films / J.M.Luther, M.Law, M.C.Beard et al. // Nano letters., –2008. T.8, № 10, –p.3488-3492.

[8] Mehdiyeva, S.I. Spectroscopıc ellıpsometry study of nanostructured PbSe thın films / S.I.Mehdiyeva, M.H.Huseynaliyev, S.N.Yasinova // International Journal on "Technical and Physical Problems of Engineering" IJTPE, Iss.48, Vol.13, No.3, –September, –2021. –p.95-98.

simple and efficient. The development of nanoscale materials with controllable dimensions and the ability to analyze the obtained dimensions and morphology is of potential importance. In addition, nanostructured materials have been extensively studied due to the uniqueness of their physical and chemical properties[9].

Thin films and powders of PbS, PbSe and $PbS_{0.5}Se_{0.5}$ were obtained by chemical bath deposition both in a solution with triethanolamine component and in a solution without triethanolamine component at room temperature, as well as at temperatures of 60°C (PbSe), 50°C ($PbS_{0.5}Se_{0.5}$) and 40°C (PbS).

In this chapter, the methods used in the measurements of PbS, PbSe and $PbS_{0.5}Se_{0.5}$ compounds selected as research objects are described. X-ray spectra of the compounds were recorded on D-8 ADVANCE and Miniflex 600 diffractometer, Raman spectra were measured on Nanofinder 30 Confocal Raman microspectrometer (Tokyo Instr., Japan). An Nd:YAG laser with a wavelength of 532 nm and a maximum power of 10 mW was used as an excitation source. The spectral resolution is 0.5 cm-1. The detector of the scattered beam was a CCD camera operating in photon collection mode (thermoelectrically cooled to -100C). Raman spectra were measured in reflection geometry. Thermogravimetric analyzes of the obtained powdered samples in the temperature range of 20-800°C were performed on the "NETZSCH STA 449 F3" device. Optical properties of PbS, PbSe and $PbS_{0.5}Se_{0.5}$ thin films were studied by the diffuse reflectance method (at room temperature) on "Nikolet IS-10" and "Vertex 70v" FTIR infrared spectrophotometers, and diffraction scattering studies of PbSe thin films were performed on "D-8 ADVANCE" X-ray diffractometer.

Morphological properties of PbS, PbSe and $PbS_{0.5}Se_{0.5}$ compounds obtained on a glass substrate were investigated using a TM-3000 Hitachi scanning electron microscope and elemental analysis was carried out.

Optical measurements “J. A. WOOLLAM COMPANY – M

[9] Nəsirov, E.F. Kimyəvi çökdürmə üsulu ilə ZnSe nano və mikro hissəciklərinin sintezi / E.F.Nəsirov //AJP FİZİKA – 2019– volume XXV– №3– s.50-54.

2000 ELLIPSOMETER" was performed on the device. With this device, it is possible to perform measurements in the spectral range of 0.74÷ 6.45 eV.

Figure 1 shows the nanostructure of the PbSe thin film obtained by chemical bath deposition at 60°C in a four-component solution and the PbSe powder obtained at 60°C in a three-component solution.

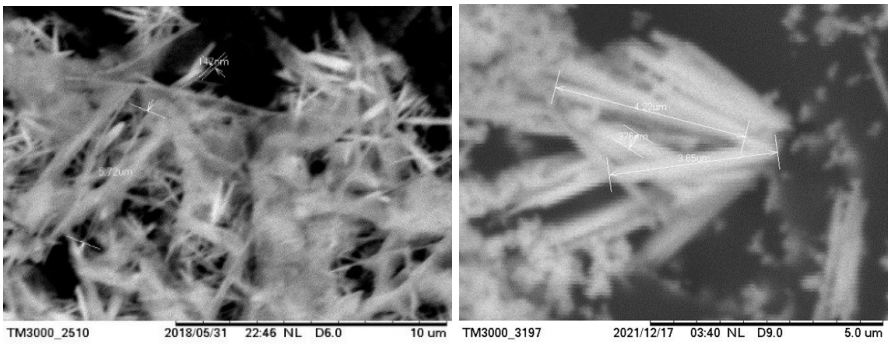


Figure 1. Nanostructure of a PbSe thin film obtained at a temperature of 60°C in a four-component solution and a PbSe powder obtained at a temperature of 60°C in a three-component solution

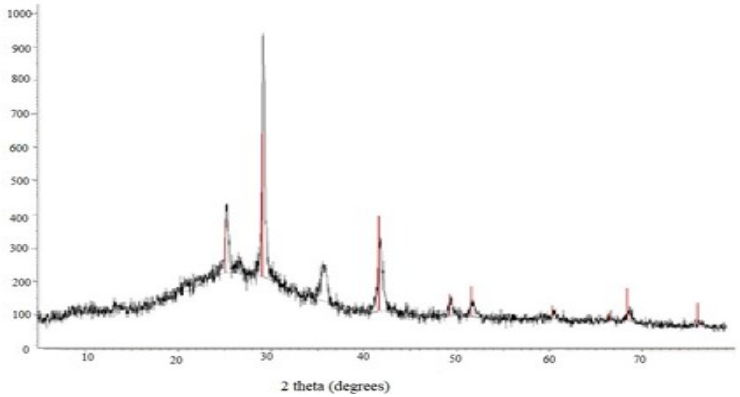
When the triethanolamine component is removed from the solution which obtained PbSe thin layer and powder by chemical bath deposition, the PbSe thin film is obtained very thin, and nanorods with a width of 376 nm and a length of 3-4 μm are observed in its powder.

Table 1

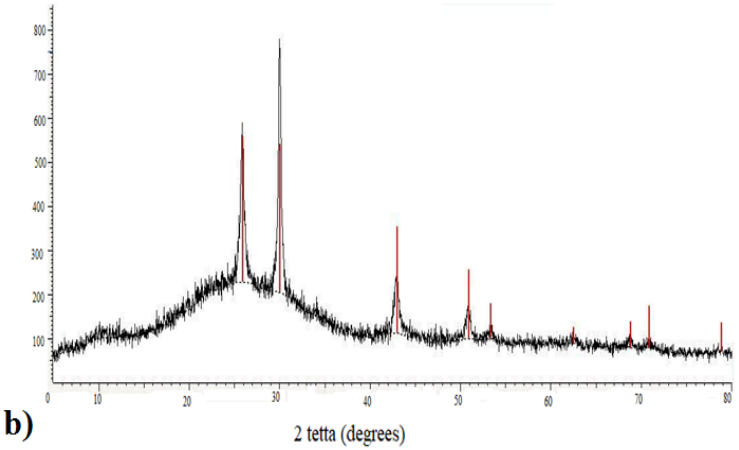
Chemical composition of PbS, PbSe and $PbS_{0,5}Se_{0,5}$ powders

	Pb	S	Se
PbS powder obtained at 40°C	40,81%	59,19 %	-
PbSe powder obtained at room temperature in solution without triethanolamine component	68,7%	-	31,3%
PbSe powder obtained at room temperature	52,95%	-	47,05%
$PbS_{0,5}Se_{0,5}$ powder obtained at room temperature	44,13%	33,14%	22,73%
$PbS_{0,5}Se_{0,5}$ powder obtained at room temperature in solution without triethanolamine component	52,78 %	25,66 %	21,56 %

In the third chapter of the dissertation, the changes in the structural properties of thin films of lead chalcogenides (PbSe and PbS) obtained by chemical bath deposition and the mechanisms affecting Raman scattering were clarified. The sizes of crystallites in PbS, PbSe and $PbS_{0,5}Se_{0.5}$ thin films were calculated using the Debye-Scherrer formula.



a)



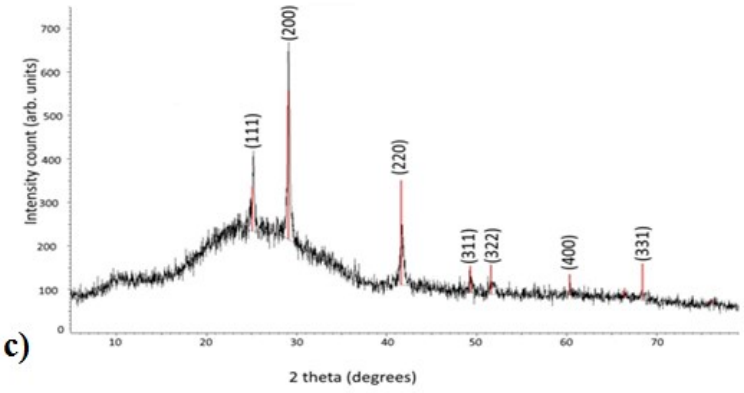


Figure 2. X-ray diffraction curves of PbSe(a), PbS(b) and $PbS_{0,5}Se_{0,5}$ (c) thin films obtained by chemical bath deposition at room temperature

The crystallite sizes of **PbSe, PbS and $PbS_{0,5}Se_{0,5}$** nanoparticles were calculated by applying the Debye-Scherrer formula to the results obtained in **Figure 2**, and the obtained results are shown in **Table 2**.

Table 2.

Parameters	**PbS**	**PbSe**	**$PbSe_{0.5}S_{0.5}$**
$2\theta_1$	25,91°	25.24°	25.22°
β_1	0,67	o.55	0.44
d_1	12,1 nm	14.8 nm	18 nm
$2\theta_2$	29,98°	29.31°	29.15°
β_2	0,7	0.77	0.46
d_2	11,7 nm	10.7 nm	17.9 nm
$2\theta_3$	42,98°	35.65°	41.65°
β_3	0,61	0.72	0.45
d_3	14,1 nm	11.6 nm	30.8 nm

The values of scattering angle (2θ) shown in Table 2 correspond to diffraction scattering from planes with Miller indices (111), (200), (220), (311), (322). As can be seen from Table 2, the crystallite sizes found in the thin layers of PbSe, PbS and $PbS_{0,5}Se_{0,5}$ are in the order of nanometers and vary in the range of 10.7 ÷ 30.8 nm. On the other hand, it is known from the obtained results that the crystallite sizes of nanoparticles change significantly when the studied substances are subjected to compositional modification. It was determined that the replacement of sulfur (S) with selenium (Se) (in full proportion) increases the crystallite size, which is calculated mainly according to the values of the scattering angle (2θ). However, the replacement of sulfur (S) with selenium (Se) in half ratio increases the crystallite size calculated for all values of the scattering angle (2θ) (2θ1, 2θ2, 2θ3).

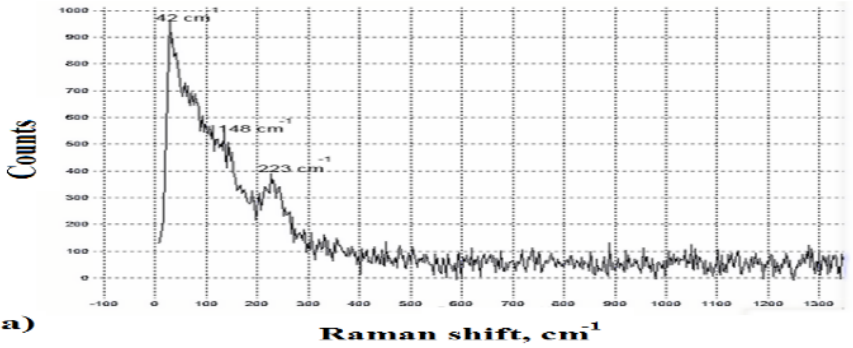
The main goal of the third chapter is to clarify the changes in the structural properties of thin layers of lead chalcogenides (PbSe and PbS) obtained by chemical bath deposition and the mechanisms of their effect on Raman scattering.

Raman scattering of light provides information about interatomic bonds, characteristic frequencies of phonons, interatomic power coefficients, phonon-phonon, phonon-electron interactions.

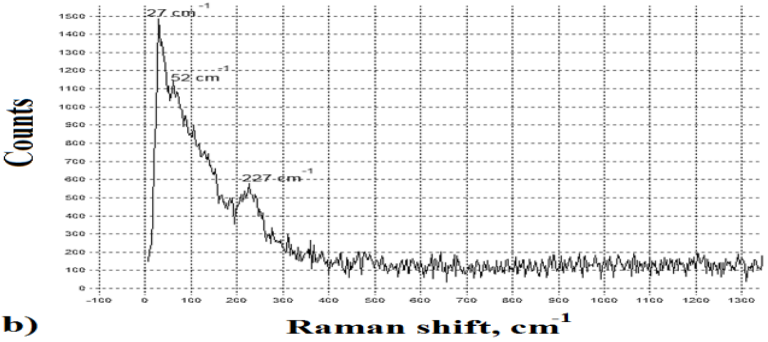
The review of literature sources shows that in volume and

nanostructured samples of lead chalcogenides, researchers determine the energy of phonons in the system by applying the Raman scattering method of light and show its connection with the chemical composition of the substance, as well as its structural properties.

From the comparative analysis of the studies, it is concluded that by changing the pH, temperature and concentration of the solution by applying the chemical bath deposition method to obtain thin films of lead chalcogenides (PbSe and PbS), it is possible to purposefully control the nano-size of crystallites, the thickness of thin films, the quality, the deposition rate, and the structure and Raman scattering properties of the substances obtained due to them.



a)



b)

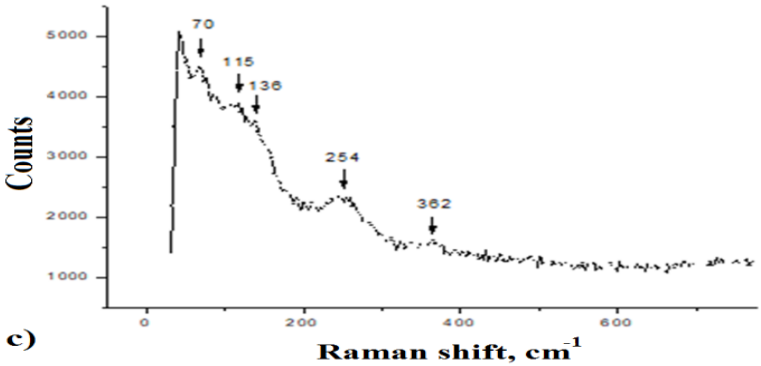


Figure 3. The Raman spectra of PbSe(a), PbS(b) and $PbS_{0,5}Se_{0,5}$ (c) thin films

Note that the shift of the scattering peak associated with transverse optical phonons to a relatively high frequency (70 cm^{-1}) is also related to the increase in the relative share of sulfur atoms inside the nanoparticles (compared to selenium), that is, it causes a decrease in the mass (μ) of the optical mode. The maximum observed in the Raman scattering spectra at ~254 cm^{-1} is associated with the presence of Se_8 rings in the scientific literature[10]. The peaks observed in the range of 120 cm^{-1}÷122 cm^{-1} indicate scattering with the joint presence of both transverse and longitudinal optical phonons. For PbS thin films obtained by the epitaxy method, the scattering due to double transverse optical phonons was observed in the frequency range of 186 cm^{-1}÷197 cm^{-1} [11]. Depending on the size of the nanoparticles, the above-mentioned scattering band is weakly observed in the obtained samples and shifts towards relatively high frequencies (223 cm^{-1}÷227cm^{-1}). Thus, the results show that either the modification of the composition or the size of the nanoparticles have a significant effect

[10] Iovu, M.S. Raman spectra of AsxSe100-x and As40Se60 glasses doped with metals / M.S.Iovu, E.I.Kamitsos, C.P. Varsamis et al. // Chalcogenide Lett, –2005. –T.2, № 3, –p.21-25.

[11] Etchegoin, P.G. Temperature dependent Raman scattering of natural and isotopically substituted PbS / P.G.Etchegoin, M.Cardona, R.Lauck et al. // Physica status solidi (b)., –2008. –T.245, № 6, –p.1125-1132.

on the photooxidation processes occurring on the surface of the obtained thin layers and the scattering bands observed in individual areas.

Researches in the **fourth chapter** show that the investigation of the mechanisms of charge transport phenomena in the case of medium and low charge density states in lead chalcogenides is of special importance from a scientific-theoretical and practical point of view. It was determined that in lead chalcogenides, when the conduction band states are not fully filled, the charge transport is explained by the mechanism of tunneling or hopping conduction between adjacent nanocrystallite layers. In particular, it was determined that it is possible to get the layers with the required conductivity properties depending on the size of nano-sized crystallites and their control mechanisms, the conditions of obtaining thin layers of lead chalcogenides (time of chemical bath deposition, temperature, pressure, chemical composition and amount of applied catalysts and solvents), which is considered one of the main directions of the presented dissertation.

Thus, the main goal of the presented paragraph of the dissertation is to investigate the mechanisms of change of conductivity properties of thin films of lead chalcogenides obtained by the chemical bath deposition method depending on the size of nano-sized crystallites and the amount of chalcogenides included in the composition. For this purpose, the temperature dependence of the electrical conductivity ($\sigma(T)$) of thin films of lead chalcogenides (PbS, PbSe, PbSSe) was measured in the temperature range T=177÷311 K and the obtained results are depicted in Figure 4, Figure 5 and Figure 6. The dependence of the logarithmic value of electrical conductivity on temperature (dependence of lnσ-on 1000/T) obeys the linear law, which shows that the dependence of electrical conductivity on temperature can be expressed by the exponential law specific to semiconductor materials.

$$\sigma = \sigma_0 \exp(-E_g \backslash kT) \qquad (1)$$

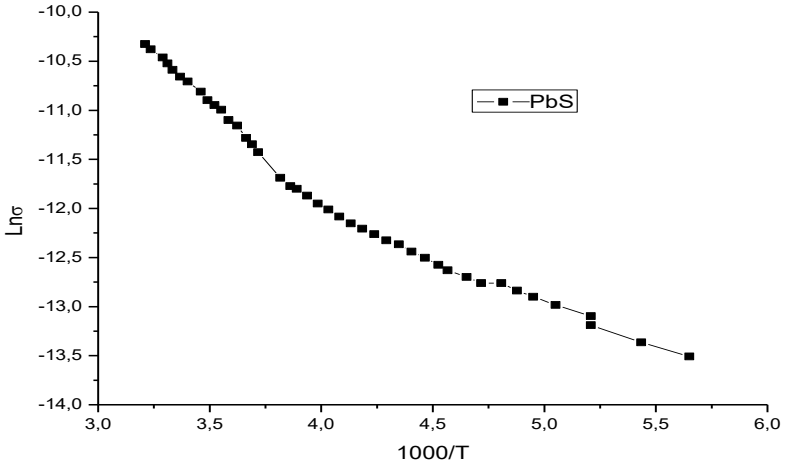


Figure 4. Temperature dependence of electrical conductivity of PbS thin film

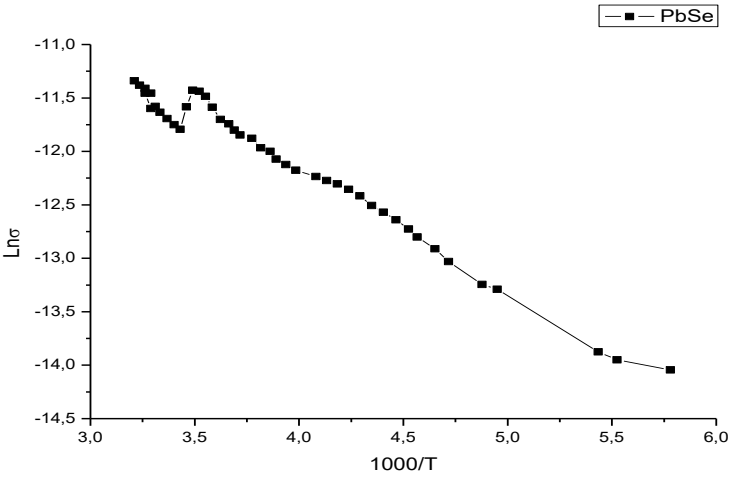


Figure 5. Temperature dependence of electrical conductivity of PbSe thin film

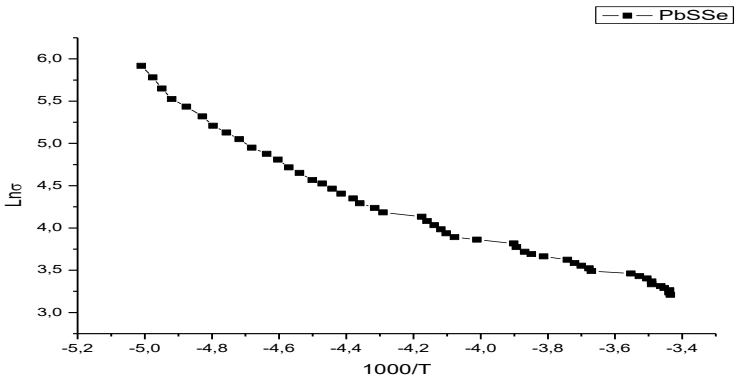


Figure 6. Temperature dependence of electrical conductivity of $PbS_{0,5}Se_{0,5}$ thin film

Knowing the inclination angle tgα of the dependence of lnσ- on 1000/T obtained as a result of the logarithmization of the formula (1), the width of the band gaps (Eg) of the studied substances was experimentally determined and the obtained results are described in Table 3. In order to comparatively analyze the change mechanisms of the experimentally determined values of the width of the band gaps (Eg) depending on the sizes of the nanosized crystallites belonging to the thin layers of lead chalcogenides obtained by the chemical bath deposition method, the results on the sizes of the nanosized crystallites calculated from the X-ray diffraction scattering curves of the corresponding compositions in Chapter 1 are also included to Table 2. In Table 3, **β**- is the half-width of the sharp maxima described in the X-ray diffraction scattering curves of the samples, and **θ** is the Bragg reflection angle. From the results described below, it can be concluded unambiguously that the width of the band gap determined by the dependence of Lnσ on 1000/T and the crystallite size of nanoparticles are exposed to change significantly as a result of subjecting to compositional modification of substances, i.e. replacing sulfur (S) with selenium (Se). A comparative analysis of the mentioned results shows that half-replacement of sulfur (S) with selenium (Se) leads to a decrease in the half-width (β) of the sharp

maxima described in the X-ray diffraction scattering curves of the samples, and an increase in the size of the nanoscale crystallites and the width of the band gap (Eg).

Table 3.

Parameters	PbS	PbSe	$PbSe_{0.5}S_{0.5}$
E_g	0,366 eV	0,292 eV	0,39 eV
β_1	0,67	0.55	0.44
d_1	12,1 nm	14.8 nm	18 nm
β_2	0,7	0.77	0.46
d_2	11,7 nm	10.7 nm	17.9 nm
β_3	0,61	0.72	0.45
d_3	14,1 nm	11.6 nm	30.8 nm

$$E_{A-B} = (E_{A-A}E_{B-B})^{1/2} + 30\,(\chi_A - \chi_B)^2 \qquad (2)$$

$$KD = 100\exp\left[-(\chi_A - \chi_B)^2/_4\right] \qquad (3)$$

In the formulas mentioned above, E_{A-A} and E_{B-B} are the energies of the homopolar bonds of the atoms included in the composition (A and B), and χ_A and χ_B are their electronegativities. As a result of the mentioned calculations, it was determined that the energy of Se-Se, Se-S and S-S bonds included in the composition of lead chalcogenides is 44 [kcal/mol], 47.4 [kcal/mol] and 50.9 [kcal/mol], respectively , and the degree of covalency of the heteropolar Se-S bond is high, KD=99.84%. When comparing the above-mentioned results with the results described in Table 3, it is concluded that the increase in the concentration of both homo and heteropolar bonds related to sulfur in the content of lead chalcogenides will lead to an increase in the average bond energy and the degree of covalency of heteropolar bonds within the nanoscale crystallites. As a result of the increase of the chemical bonding and the length of the bond, the size of the nanoscale crystallites increases, which leads to an increase in the width of the band gaps determined by the dependence of Lnσ on 1000/T in Figure 4, Figure 5 and Figure

6.

Figure 7 shows the Volt-Ampere characteristics of PbS, PbSe, $PbS_{0,5}Se_{0,5}$ thin films on a logarithmic scale.

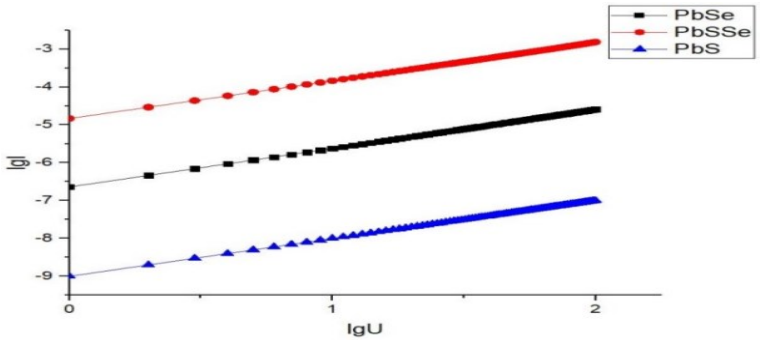


Figure 7. Volt-Ampere characteristics of PbS, PbSe, $PbS_{0,5}Se_{0,5}$ thin films obtained by chemical bath deposition

As can be seen from Figure 7, the Volt-Ampere characteristics of these connections vary with a linear (Ohm's) law (I~U).

The resistances of PbS, PbSe, $PbS_{0,5}Se_{0,5}$ thin films were as follows.

$R_{PbS} = 10^9$ Ohm

$R_{PbSe} = 4 \cdot 10^6$ Ohm

$R_{PbSSe} = 6,7 \cdot 10^4$ Ohm

In **the fifth chapter** of the dissertation, the absorption spectra of PbS, PbSe and $PbS_{0,5}Se_{0.5}$ thin films are presented, and the optical properties of PbS thin films obtained by changing the amount of triethanolamine in the solution during the chemical bath deposition process are analyzed in a comparative manner.

By establishing the $(\alpha h\nu)^2 \sim f(h\nu)$ dependencies of all three compounds, the widths of the band gaps of PbS, PbSe and $PbS_{0,5}Se_{0.5}$ thin films was determined using the Taus formula.

Figure 8 shows the optical absorption spectra of T4, N and T0 (marked 1, 2 and 3 in the figure, respectively) PbS thin films obtained by chemical bath deposition on the background of peaks of functional groups present in the infrared spectrum region (T4 and N are the thin films obtaining in triethanolamine solutions 0,24 M and 0,06 M,

respectively, T0- is a thin films obtained in the absence of triethanolamine in the mixed solution).

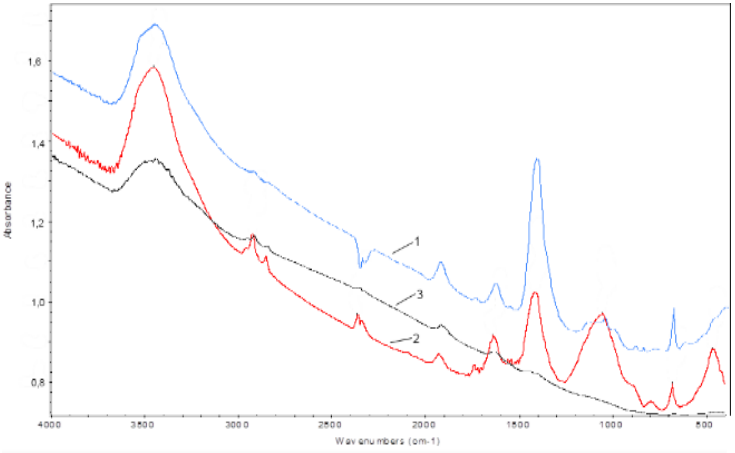


Figure 8. Optical absorption spectra (IR) of T4 (1), N (2), T0 (3) PbS thin films

After separating the absorption of only PbS compounds from the background of these peaks, the $\alpha(\hbar\nu)$dependences for PbS thin films were established (Fig. 9.).

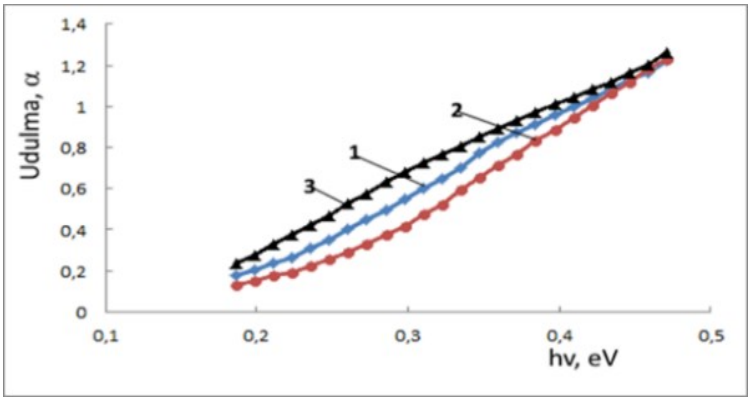


Figure 9. Optical absorption spectra of T4 (1), N (2), T0 (3) PbS thin films obtained from the background of peaks of functional groups present in the infrared region of the spectrum

Since PbS is a flat-bandgap semiconductor, the relationship $n = ½$ for this compound given from the formula $(\alpha hv)^{1/n} = A(hv\text{-}E_g)$ is true for this compound[12]. To find the width of the band gap of this combination, the dependence curves of $(\alpha\hbar\nu)^2$ on $\hbar\nu$ were constructed (Fig. 10.). From these curves, the widths of the band gaps of thin layers T4 (1), N (2), T0 (3) was determined based on the intersection of the straight line region with the abscissa axis.

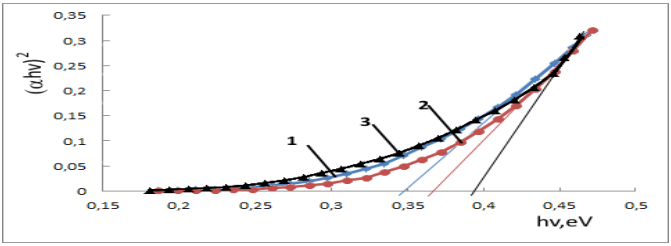


Figure 10. Calculated $(\alpha\hbar\nu)^2 \sim f(\hbar\nu)$ dependences of T4 (1), N (2), T0 (3) PbS thin films

These values were E(T4)=0.347 eV, E(N)=0.366 eV and E(T0)=0.392 eV, respectively.

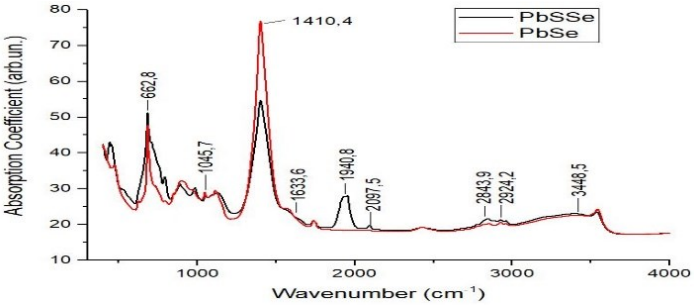


Figure 11. Optical absorption spectra of PbSe and PbS0.5Se0.5 thin films obtained at 300 K on the background of peaks of functional groups present in the infrared region of the spectrum

[12] Valenzuela-Jauregui, J.J. Optical properties of PbS thin films chemically deposited at different temperatures / J.J. Valenzuela-Jauregui, R.Ramırez-Bon, A. Mendoza-Galvan et al. // Thin Solid Films, –2003. –T.441, № 1-2, – p. 104-110.

As it is known, in the infrared region of the spectrum, a number of functional groups lead to the appearance of certain peaks in the absorption spectrum. As can be seen from the picture, almost the same functional groups are observed in both dependencies. The peak corresponding to 3448.5 cm^{-1} clearly observed in the high energy region corresponds to the O-H group of water absorbed by PbSe and PbSSe thin films, and the fact that water is absorbed by the surface is also confirmed by the presence of a peak corresponding to 1633.6 cm^{-1} of this group. The intense peak observed around 1410.4 cm^{-1} appears due to the CH_3 vibrations of the methanol used in the process. This idea was also confirmed by the presence of peaks related to CH_3 vibrations of methanol at 2924.2 cm^{-1} and 2843.9 cm^{-1}. The C-O vibrations of the methanol group give an intense peak at 1045.7 cm^{-1}.

However, it is noticeable that there is a certain difference between the FTIR spectra of these two thin films. Thus, a fairly intense peak observed at 1940.8 cm^{-1} and a peak close to it at 2097.5 cm^{-1} in $PbS_{0,5}Se_{0,5}$ are not observed in PbSe. It should be noted that these two peaks were also observed in PbS compounds and are probably related to the sulfur component.

On the background of these peaks, $\alpha(\hbar\nu)$ dependences of PbSe and $PbS_{0,5}Se_{0,5}$ thin films were established (Fig. 12.).

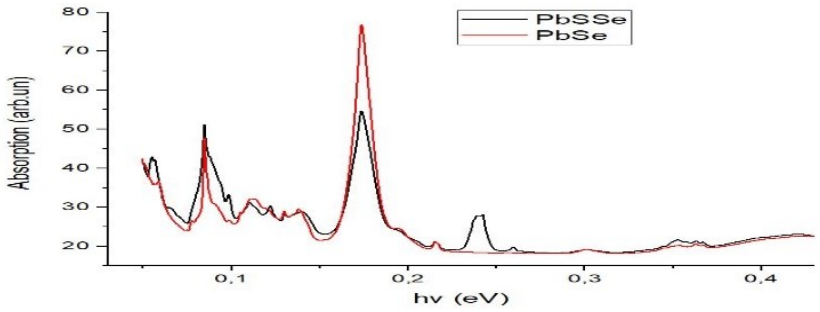


Figure 12. $\alpha(\hbar\nu)$ dependences of PbSe and $PbS_{0.5}Se_{0.5}$ thin films on the background of peaks of functional groups present in the infrared region of the spectrum

Using the Tauch formula, it is concluded that since PbS and PbSe are flat-band semiconductors[13], the relationship $n = ½$ is true for these compounds and $PbS_{0,5}Se_{0,5}$ thin films.

To find the width of the band gaps of these compounds, the dependence curves of $(\alpha\hbar\nu)^2$ on $\hbar\nu$ were constructed (figure 13.).

If the peaks of the existing functional groups are not taken into account, these dependences almost completely overlap.

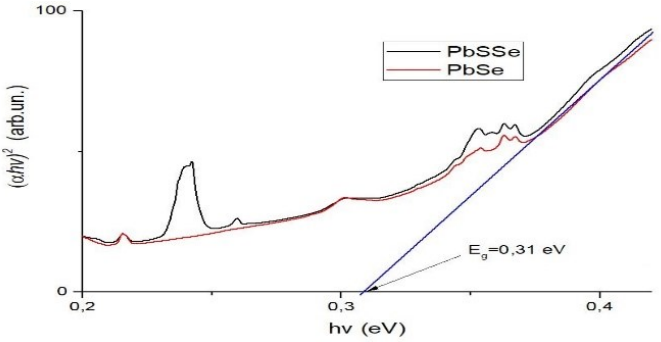


Figure 13. $(\alpha\hbar\nu)^2 \sim f(\hbar\nu)$**dependencies of** $PbS_{0,5}Se_{0,5}$ **and PbSe thin films obtained at room temperature**

Based on the intersection of the straight line area with the $(\hbar\nu)$ abscissa axis of these dependencies, it was determined that the width of the band gaps of PbSe and $PbS_{0,5}Se_{0,5}$ thin films obtained by chemical bath deposition at room temperature is the same E_g =0.31 eV.

This chapter also interprets the results of optical measurements of PbSe and $PbS_{0.5}Se_{0.5}$ thin films by the ellipsometry method. The differentiation of the experimental values of the dielectric function was used to better distinguish the structure of the interband transitions and to determine the critical points. The theoretical fitting process was performed using the "Graphical Analysis" program. The spectral dependences of the first and second order derivatives of the real and

[13] Tsai, W.T. Environmental risk assessment of hydrofluoroethers (HFEs) / W.T. Tsai // Journal of hazardous materials, –2005. –T.119, №1-3, –p.69-78.

imaginary parts of the complex dielectric function were established for both thin films. For thin films of PbSe and $PbS_{0,5}Se_{0.5}$, critical points were determined according to existing literature. In the samples of PbS, PbSe and $PbS_{0,5}Se_{0.5}$, various groups observed in the infrared region of the spectrum were functionally found to belong to the peaks corresponding to the frequencies.

This chapter is devoted to optical measurements of PbSe and PbSSe thin films. As we know, the experimental values of the $\varepsilon(\omega)$ energy dependence of the complex dielectric function obtained as a result of ellipsometric measurements are given in the form of coordinates of the energy dependence of its real and imaginary parts.

Based on these coordinates, using the “Graphical Analysis” program, energy dependence graphs of the real and imaginary parts of the complex dielectric function can be constructed.

In order to investigate the compatibility of these dependencies or their specific areas with the analytical expression given by the theory to the maximum extent, their second order derivatives are used, and these processes are performed entirely through the "Graphical Analysis" program. As a result, the constants included in these functions (4 constants) are determined. One of these constants is the *E*-critical point, which is a very important quantity for semiconductor theory.

Of course, performing the fitting process on the second order derivatives of the real and imaginary parts does not simply mean fitting on two separate dependencies and finding 4 constants separately for each. Since these two functions are the real and imaginary parts of the same complex quantity, the 4 constants sought for them in the fitting process must be the same.

Ellipsometric measurements for the nanostructured PbSe thin film were performed at 60^0 angles at room temperature.

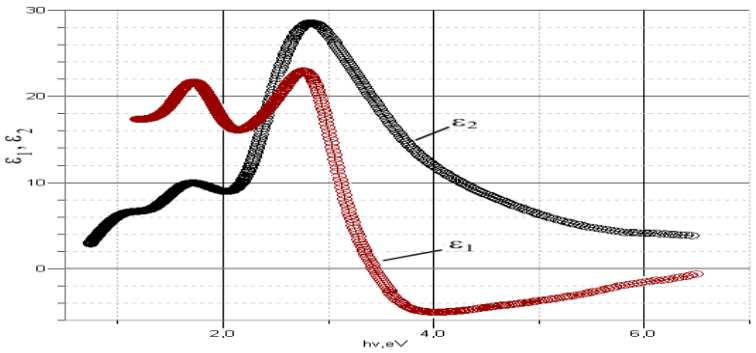


Figure 14. Spectral dependences of the $\varepsilon_1(\omega)$ is real and $\varepsilon_2(\omega)$ is imaginary parts of the complex dielectric function of a nanostructured PbSe thin film

In order to perform the fitting to the theoretical dependence, in the program "Graphical analysis" of the experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependences, the second order $d^2\varepsilon_1(\omega)/d\omega^2$ and $d^2\varepsilon_2(\omega)/d\omega^2$ derivatives were obtained and their energy dependence graphs were constructed (Fig. 15.).

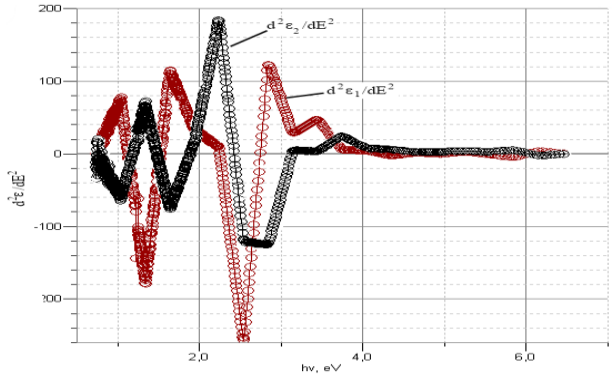


Figure 15. Spectral dependences of the $d^2\varepsilon_1(\omega)/d\omega^2$ is real and $d^2\varepsilon_2(\omega)/d\omega^2$ is imaginary parts of the second order derivative of the complex dielectric function in a nanostructured PbSe thin film

Figure 16 shows energy dependence spectra (points) of quantities $d^2\varepsilon_1(\omega)/d\omega^2$ and $d^2\varepsilon_2(\omega)/d\omega^2$ obtained from the differentiation of the $\varepsilon_1(\omega)$ is real and $\varepsilon_2(\omega)$ is imaginary experimental values of the complex dielectric function in the range of 2-3 eV. Theoretical fitting curves (full line) obtained from expression (6) based on "Graphical analysis" program are also shown here.

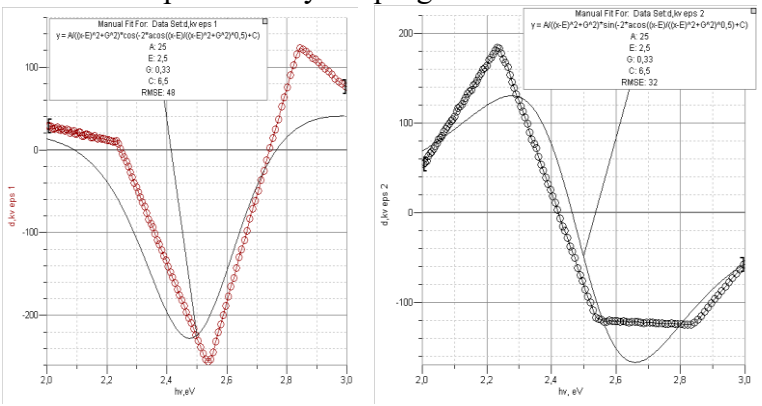


Figure 16. Second-order derivatives and best fitting curves for the 2-3 eV energy range of the PbSe thin film, based on experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies and the "Graphical Analysis" program

The best fitting case was obtained with the theoretical parameters A=25, E=2.5, Γ=0.33, and θ=0.5. The critical point value of E=2.5 eV found for the PbSe thin film is very close to the theoretically calculated value of E=2.3 eV reported in the literature and corresponds to the two-dimensional (2D) state of the critical point (m=0) and the $L_4 \rightarrow L_6$ transition[14].

The figure 17 shows the complex dielectric function of the $PbS_{0.5}Se_{0.5}$ thin film, with coordinates for over 700 points obtained

[14] Кабышев, А.В., Конусов, Ф.В., Ложников, С.Н. и др. Осаждение пленок арсенида галлия на кремнии импульсной ионной абляцией и их свойства // 9-ая Международная конференция «Взаимодействие излучений с твердым телом», –20-22 сентября –2011 г., Минск, Беларусьс, –с.306-309.

from ellipsometric measurements, along with their spectral $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies.

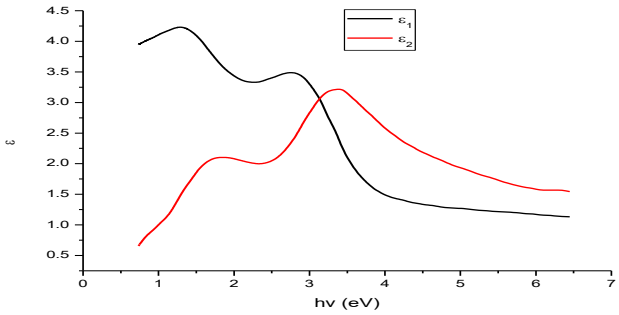


Figure 17. Spectral dependencies of the $\varepsilon_1(\omega)$ is real and $\varepsilon_2(\omega)$ is imaginary parts of the complex dielectric function of the $PbS_{0.5}Se_{0.5}$ thin film

To perform the fitting of the theoretical dependencies, second-order derivatives of $d^2\varepsilon_1(\omega)/d\omega^2$ and $d^2\varepsilon_2(\omega)/d\omega^2$ of the experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies were obtained, and their energy-dependent graphs were constructed (Figure 18).

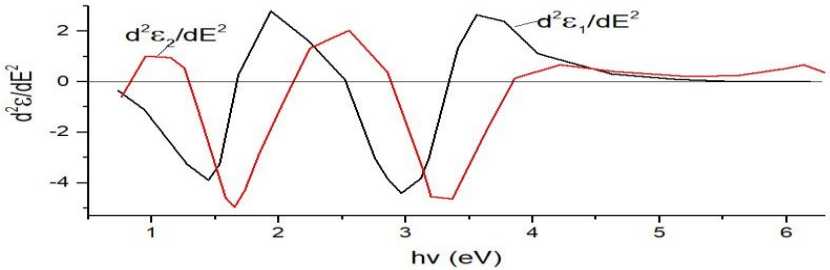


Figure 18. Spectral dependencies of the second-order derivatives of the $d^2\varepsilon_1(\omega)/d\omega^2$ is real and $d^2\varepsilon_2(\omega)/d\omega^2$ is imaginary parts of the complex dielectric function of the $PbS_{0.5}Se_{0.5}$ thin film

A careful examination of these dependencies reveals that

fitting is possible in the ranges E=0.9÷2.4 eV and E=2.5÷3.8 eV. Since the dependences $d^2\varepsilon_2(\omega)/d\omega^2$ and $d^2\varepsilon_1(\omega)/d\omega^2$ are, respectively, imaginary and real parts of the same complex function, sinusoidal and cosinusoidal relationships should be expected in their laws of variation, i.e, the imaginary $d^2\varepsilon_2(\omega)/d\omega^2$ part should lead the real $d^2\varepsilon_1(\omega)/d\omega^2$ part by π/2, which is satisfied within these ranges.

The best fitting case for the E=0.9÷2.4 eV range corresponds to a 2D-type critical point, as determined by the "Graphical Analysis" program (Figure 19).

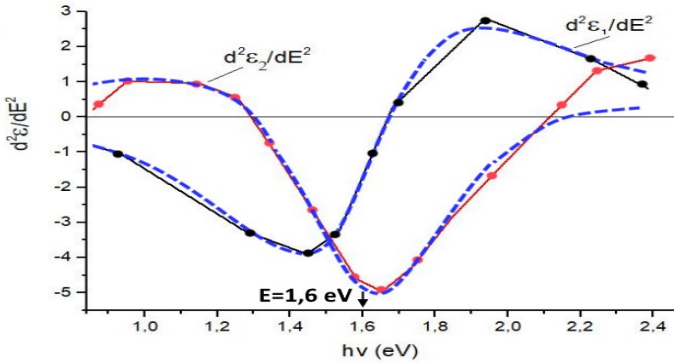


Figure 20. Second-order derivatives (points) and best fitting curves (dashed lines) for the experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies for the energy ranges E=0.9-2.4 eV of $PbS_{0.5}Se_{0.5}$ thin film, as determined using the "Graphical Analysis" program

For this range, the parameters of the analytic function were obtained as follows: A=0.89, E=1.6 eV, Γ=0.42, and θ=1.22. The RMSE errors were 0.202 for the $d^2\varepsilon_1(\omega)/d\omega^2$ and 0.846 for the $d^2\varepsilon_2(\omega)/d\omega^2$.

The value E=1.6 eV for the critical point in the band structure of $PbS_{0.5}Se_{0.5}$ thin films matches exactly with the theoretically

calculated values for both PbS and PbSe compounds [15, p. 127]. This value of the critical point in these compounds is characterized as the $L_5 \rightarrow L_7$ transition. Thus, the critical point value of E=1.6 eV in $PbS_{0.5}Se_{0.5}$ thin films also arises from the $L_5 \rightarrow L_7$ transition.

For the energy range E=2.5-3.8 eV, the best-fit case corresponds to a 1D-type ($m = -\frac{1}{2}$) critical point (Figure 18), and the parameters of the analytic function for this range were obtained as follows: A=2.5, E=3.2 eV, Γ=0.66, and θ=5. The RMSE errors were 0.625 for the $d^2\varepsilon_1(\omega)/d\omega^2$ and 0.345 for the $d^2\varepsilon_2(\omega)/d\omega^2$.

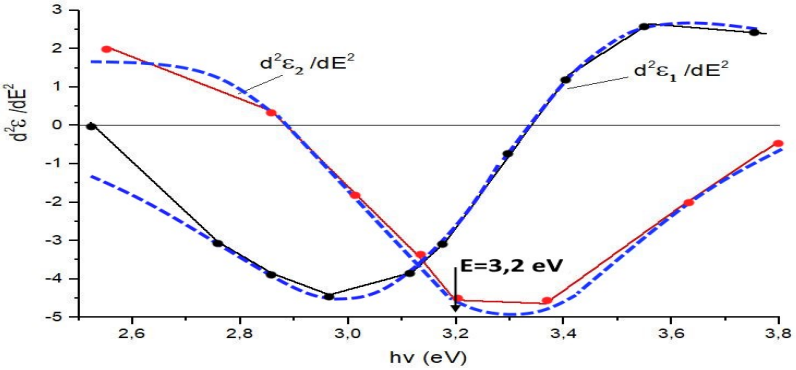


Figure 20. Second-order derivatives (points) and best fitting curves (dashed lines) for the experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ dependencies for the energy ranges E=2.5-3.8 eV of $PbS_{0.5}Se_{0.5}$ thin film, as determined using the "Graphical Analysis" program

Based on literature data and theoretical calculations, the energy values E=3.5 eV and E=2.9 eV, corresponding to the M2 state in PbS and PbSe, respectively, have been identified. These values are associated with the $\Delta_5 \rightarrow \Delta_6$ transition[14].

THE MAIN RESULTS:

1. Depending on the amount of triethanolamine in the solution and the temperature, a technology for obtaining thin films of lead chalcogenides (PbS, PbSe, and $PbS_{0,5}Se_{0,5}$) by chemical deposition was developed. As a result of microscopic studies, the optimal dimensions of the samples were found to be l~5÷6 μm, d~150÷376 nm, revealing the presence of nanorods.

2. Using the ellipsometric spectroscopy method, the real and imaginary parts of the dielectric constant for PbS, PbSe, and $PbS_{0.5}Se_{0.5}$ were measured. Analysis of critical points was performed with the help of the "Graphical Analysis" program, revealing that the best fitting occurs at a two-dimensional (2D) critical point (m=0) in the 2-3 eV range. The experimentally determined energy value of E~2,38 eV is close to the theoretically calculated value of E~2,30 eV, corresponding to the transition from $L_4 \rightarrow L_6$ in the Brillouin zone.

3. In the X-ray diffraction spectra of thin films of PbS, PbSe, and $PbS_{0.5}Se_{0.5}$, the 2θ angles are consistent. However, for PbS, these angles shift slightly towards smaller values. The difference in the angles of the peaks corresponding to the (111) planes of $PbS_{0.5}Se_{0.5}$ and PbS is 2θ=0.9˚, but as the angles increase, this difference gradually decreases, reaching 2θ=3˚ for the peaks corresponding to the (422) planes.

4. It has been shown that the peaks observed at 135 cm^{-1} and 47.6 cm^{-1} in the Raman scattering spectrum of PbSe are associated with longitudinal and transverse optical phonons, respectively. Peaks observed in the frequency range of 42 sm^{-1}÷ 52 sm^{-1} can be explained by transverse optical phonons that are Raman-active in the (111) plane.

The shift of these peaks to relatively higher frequencies (70 cm^{-1}) in the Raman scattering spectrum, due to half-substitution of selenium with sulfur, is related to the increase in the crystalline size of the nanoparticles that facilitate scattering in the (111) plane. Additionally, due to the higher chemical activity and bonding energy of sulfur atoms, the bonding connectivity within the nanoparticles is strengthened. As a result, the force constant (k) increases, which, according to the molecular structure model, leads to an increase in the frequency of Raman-active vibrational modes. This increase results in a shift of the scattering peak

associated with transverse optical phonons to relatively higher frequencies.

5. It has been shown that the ~254 cm^{-1} peak observed in the Raman scattering spectrum of $PbS_{0.5}Se_{0.5}$ samples corresponds to scattering from virtual vibrational states of Se_8 rings, while the peaks observed in the frequency range of 120 cm^{-1} ÷ 122 cm^{-1} are associated with scattering from combined vibrations of transverse and longitudinal phonons.

6. It has been determined that, as a result of the half-substitution of selenium with sulfur, the growth of nanoparticle sizes increases the bonding connectivity and force constant (k) within the nanoparticles due to the high chemical activity and bonding energy of sulfur atoms. This results in an increase in the frequency of Raman-active vibrational modes, ranging from 42 cm^{-1} to 70 cm^{-1}.

7. It has been found that an increase in the concentration of sulfur-related homo- and heteropolar bonds in lead chalcogenides leads to an increase in the average bonding energy within nanoscale crystals, the degree of covalency of heteropolar bonds, chemical bonding connectivity, bond length, the size of nanoscale crystals (d = 10.7 nm to 30.8 nm), and the band gap width (Eg = 0.292 eV ÷ 0.39 eV).

8. It has been shown that thin films of PbS, PbSe, and $PbS_{0.5}Se_{0.5}$ nanoparticles, obtained by the chemical bath deposition method, have a relatively low absorption coefficient in the mid-infrared region of the spectrum, which suggests potential applications in passive fiber optics.

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