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Formation of PbS microstructured films by CBD method and study of structural properties

G. Amirbekova[a], Zh. Tolepov[a,*], N. Guseinov[a], R. Nemkaeva[a], T. Kuanyshbekov[b], A. Ramazanova[a], D. Tlaubergenova[a]

[a]*Department of Physics and Technology, Al-Farabi Kazakh National University, Al-Farabi Avenue, 71, Almaty 050040 Kazakhstan*

[b]*National Scientific Laboratory of Collective Use S. Amonzholov East Kazakhstan University, 55 Kazakhstan str., Ust-Kamenogorsk 070002, Kazakhstan*

Microcrystalline lead sulfide (PbS) films were synthesized using the chemical deposition method. The films were deposited on pre-cleaned glass substrates and polished silicon wafers. Chemicals of high purity were utilized in the process. The morphology, composition, and structure of the films were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The films exhibited a galena phase with a face-centered cubic structure belonging to the Fm-3m space group. The average grain size was determined using the Williamson-Hall method, revealing a homogenous structure. Raman spectroscopy further confirmed the structural integrity of the films. The obtained results contribute to the understanding of the synthesis and properties of microcrystalline PbS films.

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1. Introduction

Lead sulfide (PbS) is a widely studied p-type semiconductor with versatile applications, owing to its tunable optical and electrical properties. Its narrow bandgap (0.41 eV) and exciton Bohr radius (18 nm) make it a valuable material for various fields. PbS has found success in infrared sensors due to its unique properties, leading to the development and manufacture of high-performance devices. Additionally, PbS plays a crucial role in the production of photovoltaic cells for solar energy applications [1], [2].

Furthermore, PbS nanoparticles are employed to harness solar energy for chemical processes. Notably, PbS film-based gas sensors exhibit sensitivity to NO_2 and NH_3 compounds at room temperature. The distinctive electronic characteristics of PbS extend its utility to optoelectronic systems, including infrared photodetectors, optical switches, photoelectronics, electroluminescence, hotoluminescence, and displays, as well as thermoelectronic devices [3]–[5].

At the nanoscale, PbS nanocrystals hold a significant position in optoelectronics, exhibiting distinct structural, optical, and electronic properties compared to bulk materials. Alloying PbS with other materials allows for the creation of semiconductors with tailored properties, offering new opportunities for applications. In recent years, advancements in nanoscience and nanotechnology have greatly enhanced our understanding and manipulation of PbS at the nanoscale, revealing its full potential [6]–[9].

This work explores the production of lead sulfide using the chemical bath deposition method, with a focus on determining a crucial parameter for cost-effectiveness and process simplicity.

* Corresponding author: mr.tolepov@mail.ru
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2. Material preparation

Microcrystalline lead sulfide films were obtained using the chemical bath deposition method onto pre-cleaned glass substrates and polished silicon wafers with dimensions of approximately 1 cm². In the production of microcrystalline films, chemicals of high purity (more than 99%) were utilized: Pb $(NO_3)_2$ (lead nitrate), NaOH (sodium hydroxide), and CH_4N_2S (thiourea) from Sigma-Aldrich (USA). It is worth noting that the sequence of mixing chemical solutions played a crucial role in forming microcrystalline lead sulfide films.

In the first stage, the solutions of Pb $(NO_3)_2$ (lead nitrate) 25 mL 0.18 M (1.52 g) and NaOH (sodium hydroxide) 75 mL 0.38 M (1.151 g) were stirred using a magnetic stirrer for 60 minutes at a temperature of 70°C in a 150 mL beaker. Importantly, at this temperature, the solutions mix uniformly. An aqueous solution of CH_4N_2S (thiourea) 50 mL 0.11 M (0.398 g) was stirred for 60 minutes at room temperature. In the second stage, to avoid rapid precipitation, the aqueous solution of thiourea was carefully poured into the lead nitrate and sodium hydroxide solution. During the first 20 minutes, the solution darkened from a transparent state to the formation of a dark gray film on the wall of the beaker. The pH value was maintained around 12 to 14. Substrates were vertically immersed in the solution during stirring. The film growth on the substrates took 35 minutes. Subsequently, the obtained films were cleaned in an ultrasonic bath. Figure 1 illustrates the sequence of stages in obtaining microcrystalline lead sulfide films.

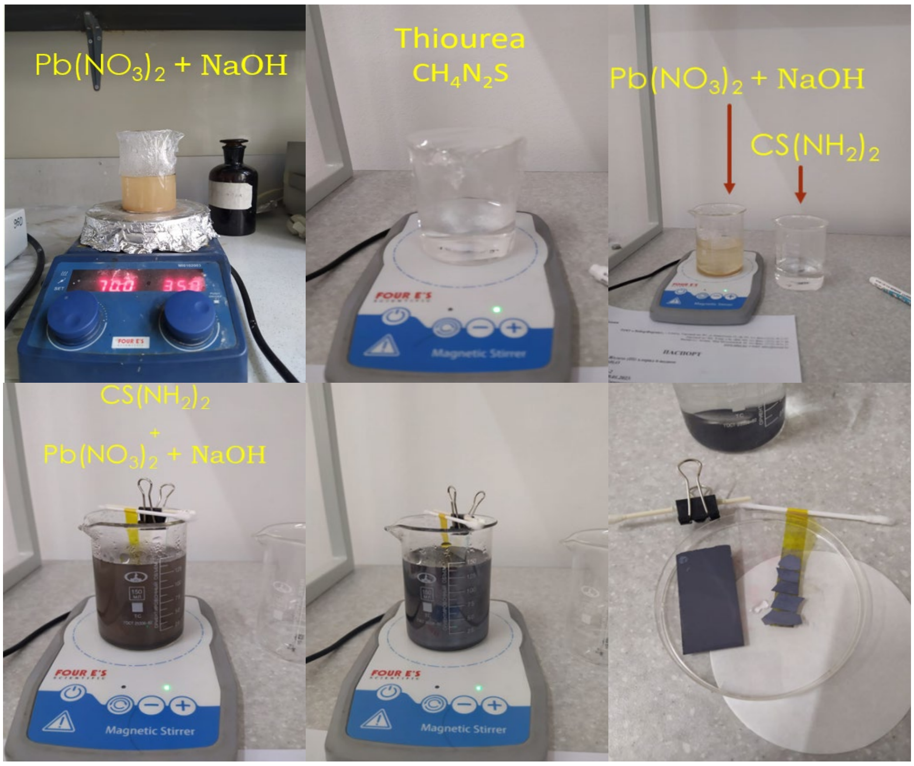

Fig. 1. Stages of obtaining microcrystalline lead sulfide films by the chemical deposition method from an aqueous solution.

3. Results and discussion

The composition and morphology of microcrystalline lead sulfide films were studied using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) with an FEI Quanta 3D 200i instrument.

Figure 2 presents the morphology and composition of microcrystalline lead sulfide films. In Figure 2 (a), it can be observed that the films have a rough surface consisting of cubic-shaped grains. The results of energy-dispersive analysis reveal that the stoichiometric ratio corresponds to the molecular unit PbS, with a deviation not exceeding 1.5%.

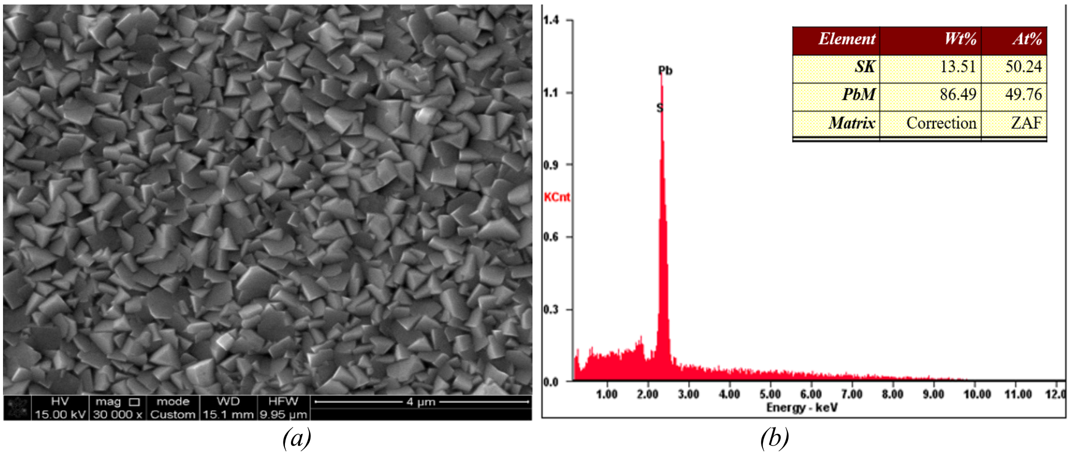

Fig. 2. (a) Morphology and (b) EDS analysis of microcrystalline lead sulfide films.

The structure of the obtained samples was studied using the Rigaku MiniFlex 600 X-ray diffractometer.

Figure 3 shows the result of X-ray structural analysis of microcrystalline lead sulfide films. From the figure, it can be inferred that the lead sulfide films possess a galena phase, which means a face-centered cubic structure belonging to the Fm-3m space group. The lattice constant is determined to be 5.93 Å.

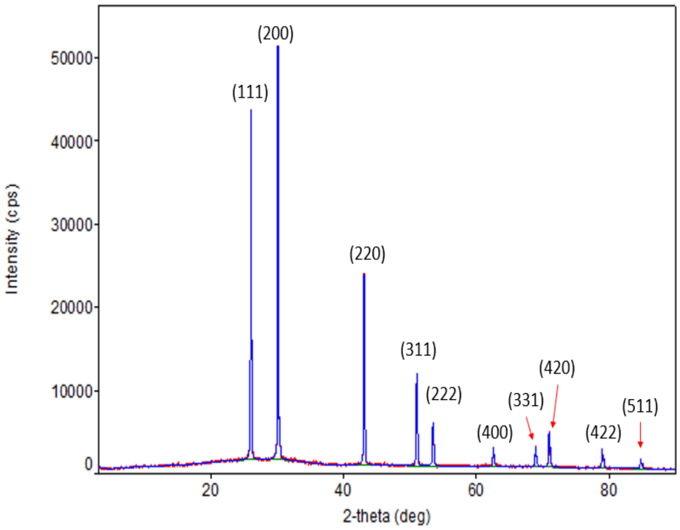

Fig. 3. XRD pattern of microcrystalline PbS thin films.

Next, the average grain size was determined using the Williamson-Hall method based on the uniform deformation model. In Figure 3, the dependence of (β cos θ) on sin θ is shown, where β is the sum of the broadening parameters due to size and strain, and θ is the Bragg angle. The coefficient of determination of the linear fit corresponds to a value of 0.98. By intersecting the linear fit with the Y-axis, the average grain size was determined to be 79.5 nm. The gradient of the linear fit indicates the strain, which is $74 \cdot 10^{-3}$ %. The model aligns well with the experimental points, indicating the homogeneity of the structure[10], [11].

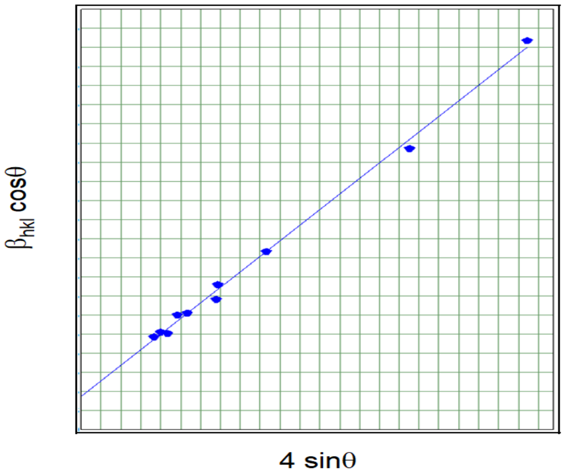

Fig. 4. Williamson – Hall plot.

The investigation of the structure using Raman spectroscopy was conducted on the Solver Spectrum 600/600 spectrometer. The wavelength of the laser emission was 632 nm with a power of 0.05 mW. In Figure 5, the Raman spectrum decomposition is shown by peaks: 129 ± 3, 174 ± 3, 262 ± 3, 323 ± 3, 425 ± 3 cm^{-1}, corresponding to the vibrational modes LO, TO, 2TO, 1 LO, 2 LO, where the peak at 965 ± 3 cm^{-1} is associated with the photodegradation of lead sulfide [12], [13].

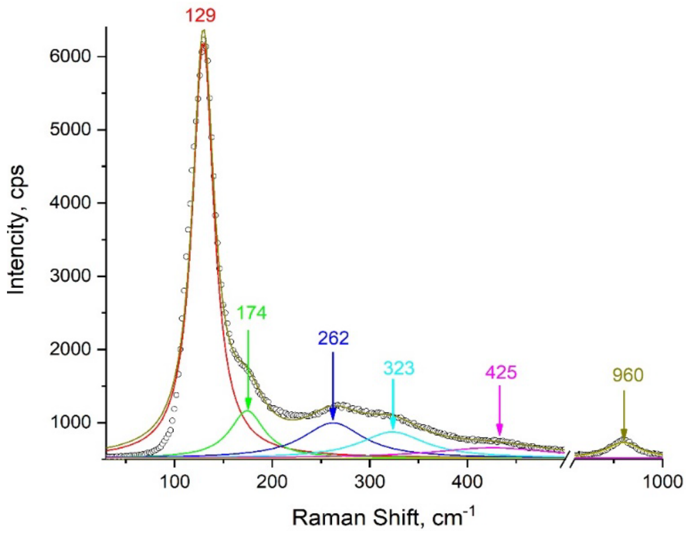

Fig. 5. Raman spectra of nanocrystalline PbS thin film.

4. Conclusion

In this study, microcrystalline lead sulfide films were successfully synthesized through chemical deposition. The comprehensive analysis of the films' morphology, composition, and structure was carried out using SEM, EDS, XRD, and Raman spectroscopy. The films demonstrated a galena phase with a face-centered cubic structure, exhibiting good structural integrity. The calculated average grain size provided insights into the nanocrystalline nature of the films. The research confirms that the melting temperature of thiourea plays a crucial role in the formation of lead sulfide nanostructured films. This temperature parameter significantly impacts the structure of the obtained material, making it a key factor in the synthesis and control of lead sulfide nanostructures.These findings offer valuable information for the development and applications of microcrystalline PbS films in various fields, including electronics, optics, and materials science.

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