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# **Original articles**

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# Deposition of lead sulfide films from "Pb( $CH_3COO$ )<sub>2</sub> – $N_2H_4CS$ " aqueous solutions and their properties

# E. A. Gannova, M. V. Grechkina, V. N. Semenov, A. N. Lukin, S. A. Ivkov, T. V. Samofalova<sup>∞</sup>

Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

### Abstract

The article presents the results of the study of lead sulfide films obtained by the aerosol pyrolysis of solutions of complex compounds of lead acetate and thiourea at temperatures of 300 and 400 °C. The concentration areas of existence of lead (II) hydroxo complexes were determined. We determined the domination regions of  $[Pb(N_2H_4CS)_4]^{2+}$  complexes, which are precursors during the deposition of lead sulfide films.

The crystal structure, phase composition, and surface morphology of the synthesized films were studied by X-ray phase analysis and atomic force microscopy. It was found that under these deposition conditions, the crystallized PbS films have a cubic structure and are textured in the (200) crystallographic direction. When the concentration of thiourea in the initial solution increases, there is an increase in the values of the average and root-mean-square roughness, as well as the relief height difference of the synthesized samples.

PbS films obtained at a temperature of 400 °C are characterized by a denser packing of grains and a perfect surface microstructure. By optical spectrophotometry, we determined the band gap of synthesized PbS, which is from 0.41 to 0.45 eV for direct allowed transitions.

**Keywords**: PbS films, Aerosol pyrolysis method, Atomic force microscopy, Thiourea complex compounds, X-ray phase analysis, Transmission spectra

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🖂 Samofalova T. V., e-mail: TSamofalova@bk.ru



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E. A. Gannova et al.

Deposition of lead sulfide films from "Pb(CH<sub>z</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " aqueous solutions...

## 1. Introduction

Films of lead sulfide, which is a narrowbandgap semiconductor, are widely used as for creating efficient photovoltaic converters, photodetectors, and photoresistors, temperaturesensitive sensors, IR detectors in the infrared region of the spectrum [1-5]. An urgent task is to synthesize PbS films with a given crystal structure and variable properties. The main methods for obtaining lead sulfide layers are chemical synthesis methods, such as chemical deposition and aerosol pyrolysis from solutions of sulfur-containing precursors [6–10]. Varying the crystal structure, optical and electrophysical properties of sulfide films provides an economical and technically accessible method for the aerosol pyrolysis of solutions of thiourea complex compounds (TCCs). The main idea of the method is the thermal destruction of complex compounds with the formation of a solid phase of metal sulfide [11, 12]. The aim of this work was to study the process of deposition of lead sulfide thin films by the aerosol pyrolysis of aqueous solutions of "Pb(CH<sub>3</sub>COO)<sub>2</sub> –  $N_2H_4CS$ ", as well as to analyze the surface morphology, phase composition, and optical properties of the synthesized layers.

# 2. Experimental

To produce complex compounds and to deposit PbS films, we used chemically pure  $Pb(CH_3COO)_2 \cdot 3H_2O$  and extra pure  $N_2H_4CS$  (thiourea). The concentration of the metal salt in the sprayed solution was 0.1 mol/l, the concentration of thiourea was between 0.4 and 1 mol/l. PbS films were obtained by the aerosol pyrolysis of aqueous solutions of "Pb(CH<sub>3</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " on a heated substrate at temperatures of 300 and 400 °C. The substrates were silica plates, which were prewashed in nitric acid and chromic mixture, then washed repeatedly in distilled water. Each sample was sprayed for 1 minute.

X-ray phase analysis was carried out on a DRON 4-07 X-ray diffractometer with CuK $\alpha$ -radiation at the X-ray tube accelerating voltage of 29 kV and an anode current of 26 mA. The phase composition of the films was determined by comparing the experimental values of interplanar distances  $d_{\rm hkl}$  obtained from diffraction patterns with reference data [13]. We studied the surface morphology of the samples using a SOLVER P47 atomic force microscope, analyzing the following parameters: arithmetic mean deviation of the surface profile  $R_a$ , RMS roughness, relief height difference  $\Delta$ , and height of the largest number of grains h. In this study, we used Etalon series HA\_FM composite polysilicon cantilevers by TipsNano with a curvature radius of 10 nm and gold reflective coating.

The transmission spectra of PbS films were measured using a Vertex 70 Fourier spectrometer on a quartz substrate in the range of wavenumbers from 7000 to 2500 cm<sup>-1</sup>. To determine the optical band gap  $E_g$ , we used the Tauc formula for direct allowed transitions [14, 15]:

$$(\alpha d)_n = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu}, \qquad (1)$$

where hn is the photon energy, d is the sample thickness, and  $\alpha$  is the absorption coefficient. Considering the non-uniformity of the thickness of the studied films within the analyzed dimensions, we normalized the transmission spectra [16]:

$$(\alpha d)_n = \frac{(\alpha d)_{h\nu} - (\alpha d)_{\min}}{(\alpha d)_{\max} - (\alpha d)_{\min}}$$
(2)

The band gap was determined by extrapolation of the linear parts of the dependences  $((\alpha d)_n hn)^2 = f(hn)$  to zero. The experimental data were processed using Origin Pro 8.5.

## 3. Results and discussion

During the deposition of metal sulfide films by the aerosol pyrolysis of solutions of thiourea complex compounds, the processes leading to the formation of sulfide on a heated substrate begin already in the initial solution. They start with the formation of a covalent bond between the lead cation and the sulfur atom  $(NH_2)_2CS$ [10, 17]. Therefore, in order to understand the deposition mechanism of PbS layers, we studied ionic equilibria in the "Pb(CH<sub>3</sub>COO)<sub>2</sub> – N<sub>2</sub>H<sub>4</sub>CS" solution taking into account the stability constants of different complexes. We determined the optimal concentration areas of thiourea complexes ( $C_{TU} = 5 \cdot 10^{-1} \text{ mol/l}$ ,  $C_{Pb}^{2+} = 5 \cdot 10^{-4} \text{ mol/l}$ ), which are sulfide precursors. Condensed Matter and Interphases / Конденсированные среды и межфазные границы 2024;26(2): 238–246

#### E. A. Gannova et al.

Deposition of lead sulfide films from "Pb(CH<sub>3</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " aqueous solutions...

Comparing the stability constants of lead complexes (II) in aqueous solutions [18], it can be noted that the highest values are for hydroxo complexes. Therefore, when analyzing the "lead salt – thiourea" solution, we first considered the hydrolysis process as complexation, in which hydroxyl ions are incoming ligands.

We calculated the fractions of hydroxo complexes in the "lead salt – thiourea" system at the initial concentration of  $C_{\rm pb}^{2+} = 1 \cdot 10^{-2}$  mol/l (in this case, the Pb(OH)<sub>2</sub> precipitation does not occur) using the formulas in [11]. As can be seen from the calculated distribution diagram (Fig. 1), the pH at the beginning of the formation of Pb<sup>2+</sup> hydroxo complexes is 4.5 (their fraction in the solution is 0.03 %). The concentration of hydroxo complexes increases sharply with increasing pH. In this case, it is possible to suppress hydrolysis in the solution by an excess of thiourea. Thus, the hydroxo groups are replaced with thiourea molecules in the inner sphere of the complex compound.

To model the initial solution taking into account the formation of thiourea complexes, we calculated and built three-dimensional diagrams and cross section lines of equal fractions. The methodology for their construction is provided in [19]. For the calculation, we used the experimental stability constants of homoligand complexes [18], the constants for mixed-ligand complexes were calculated using the formula [11]



а

 $\lg K_{ij} = \frac{i \lg K_{im} + j \lg K_{jm}}{i+j} + \lg \frac{m!}{i!j!}.$ 

Here  $K_{ij}$  is the stability constant of the mixed [PbTU<sub>i</sub>(CH<sub>3</sub>COO)<sub>j</sub>] complex (j + j = m),  $K_{im}$  and  $K_{jm}$  are the stability constants of the homogeneous complexes [Pb(TU)<sub>m</sub><sup>2+</sup>] and [Pb(CH<sub>3</sub>COO)<sub>m</sub><sup>2-m</sup>], respectively, and  $\frac{m!}{i!j!}$  are the comproportionation

constants.

Thus, we determined the domination areas of thiourea complex compounds, which are precursors during the deposition of lead sulfide films. Fig. 2 shows the three-dimensional diagram and the cross section lines of equal fractions for



Fig. 1. Distribution diagram of lead (II) hydroxo complexes



**Fig. 2.** Three-dimensional distribution diagrams (a) and cross section lines of equal fractions (b) for the  $[Pb(N_2H_4CS)_4]^{2+}$  complexes in the "Pb(CH<sub>3</sub>COO)<sub>2</sub> – N<sub>2</sub>H<sub>4</sub>CS" system

E. A. Gannova et al.

Deposition of lead sulfide films from "Pb(CH<sub>2</sub>COO)<sub>2</sub> – N<sub>2</sub>H<sub>4</sub>CS" aqueous solutions...

"Pb(CH<sub>3</sub>COO)<sub>2</sub> – N<sub>2</sub>H<sub>4</sub>CS" aqueous solutions of the [Pb(N<sub>2</sub>H<sub>4</sub>CS)<sub>4</sub>]<sup>2+</sup> complex.

In the "Pb( $CH_3COO$ )<sub>2</sub> – N<sub>2</sub>H<sub>4</sub>CS" aqueous solution, a complex compound is formed, in which thiourea enters the inner sphere, and it binds to the metal cation by a donor sulfur atom already in the initial solution [9]. This is how the fragments of the sulfide structure are formed in the inner sphere of the complex compound obtained in the sprayed solution by the interaction of the lead salt and N<sub>2</sub>H<sub>4</sub>CS. When the thiourea complex compound decomposes on a heated substrate, the most thermally stable product, PbS, is released.

When determining the structure of PbS films, we obtained diffraction patterns in the form of dependence of the diffracted radiation intensity on spatial coordinates for samples synthesized at different concentration ratios of lead acetate and thiourea. The obtained diffraction patterns are shown in Fig. 3. The halo, which appears on the diffraction patterns of each film in the range of angles from 15 to 25°, refers to the amorphous structure of the cuvette on which the samples were placed during imaging.

The X-ray phase analysis data (Table 1) suggest that the deposited PbS films crystallize in a cubic structure of the *B1* type (space group). The values of interplanar distances of experimentally obtained lead sulfide films are close to the values of the reference polycrystalline lead sulfide. We obtained its diffraction pattern using the same diffractometer with the same imaging parameters. Table 2 shows that the deviations of the values of interplanar distances of the etalon and lead sulfide thin films are much smaller than the error limit of the device. This indicates the high quality of the synthesized lead sulfide layers.

For all studied PbS films, the interplanar distances for each crystallographic plane *hkl* practically coincide with each other, and the intensities of the same diffraction maxima are different (Table 1, Fig. 3). All the diffraction patterns show the highest intensity at the reflection (200), and the half-width of this peak



**Fig. 3.** Diffraction patterns of PbS films obtained at different temperatures and component ratios of  $C(Pb(CH_zCOO)_2):C(N_2H_zCS)$ 

Condensed Matter and Interphases / Конденсированные среды и межфазные границы 2024;26(2): 238-246

	E. A. Gannova et al.	Deposition of lead sulfide films from "	Pb(CH,COO)	– N <sub>3</sub> H <sub>4</sub> CS" aqueous solutions
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	Depositio	Database [13]					
		300 °C		400	°C	1 %	h k l
~	1:6	1:8	1:10	1:8	1:10	и, А	
d,	3.4205	3.4205	3.4205	3.4205	3.4205	3.4260	111
ane distance	2.9640	2.9640	2.9592	2.9592	2.9640	2.9670	200
	2.0964	2.0964	2,0964	2.0964	2.0964	2.0980	220
	1.7874	1.7874	1.7890	1.7890	1.7874	1.7890	311
	1.7112	1.7127	1.7127	1.7127	1.7127	1.7130	222
pla	1.4828	1.4828	1,4828	1.4817	1.4828	1.4830	400
Inter	1.3602	1.3610	1.3602	1.3602	1.3602	1.3610	331
	1.3259	1.3267	1.3267	1.3259	1.3267	1.3270	420
	1.2100	1.2100	1.2119	1.2113	1.2113	1.2110	422

**Table 1.** Characteristics of the interplanar distances of the deposited PbS films compared with

Table 2. Comparison of the interplanar distances of experimental samples with the lead sulfide standard

_ 1	Stan-	Deposition temperature 300°C						Deposition temperature 400°C			
Peak dard PbS	dard PbS	PbS		PbS		PbS		PbS		PbS	
number [13]		1:6		1:8		1:10		1:8		1:10	
	d, Å	d, Å	$\Delta d, Å$	d, Å	$\Delta d, \text{\AA}$	d, Å	$\Delta d, Å$	d, Å	$\Delta d, Å$	d, Å	$\Delta d, Å$
1	3.4205	3.4205	0	3.4205	0	3.4205	0	3.4205	0	3.4205	0
2	2.9640	2.9640	0	2.9640	0	2.9592	0.0048	2.9640	0	2.9592	0.0048
3	2.0964	2.0964	0	2.0964	0	2.0964	0	2.0964	0	2.0964	0
4	1.7874	1.7874	0	1.7874	0	1.7890	0.0016	1.7874	0	1.7890	0.0016
5	1.7112	1.7112	0	1.7127	0.0015	1.7127	0.0015	1.7127	0.0015	1.7127	0.0015
6	1.4828	1.4828	0	1.4828	0	1.4828	0	1.4828	0	1.4817	0.0011
7	1.3610	1.3602	0.0008	1.3610	0	1.3602	0.0008	1.3602	0.0008	1.3610	0
8	1.3267	1.3259	0.0008	1.3267	0	1.3267	0	1.3267	0	1.3259	0.0008
9	1.2113	1.2100	0.0013	1.2100	0.0013	1.2119	0.0006	1.2113	0	1.2113	0
10	1.1416	1.1421	0.0005	1.1421	0.0005	1.1416	0	1.1421	0.0005	1.1421	0.0005
11	0.9895	0.9892	0.0003	0.9892	0.0003	0.9895	0	0.9902	0.0007	0.9888	0.0007

was the same for all samples. In general, this may indicate the preferential orientation of crystallites in this direction. Changing the molar ratio of components in the "Pb(CH<sub>3</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " system did not change the phase composition and crystal structure of the formed lead sulfide films. In the case of hydrochemical deposition, PbS layers with a cubic structure were also formed [20–22].

Previous studies [23–25] have showed that PbS films can crystallize in a cubic structure close to the  $D0_3$  type, with a partially disordered (statistical) distribution of sulfur atoms over octahedral and tetrahedral positions. Since in the lead sulfide lattice the octahedral positions of the *B*1 structural type are predominantly occupied, a highly defective *B*1 structure with a high concentration of sulfur vacancies in regular octahedral positions and interstitial sulfur atoms in tetrahedral positions is formed [23, 24].

We studied the surface morphology of PbS films and obtained surface scans of the samples in the semi-contact mode of atomic force microscopy (AFM). Fig. 4 shows AFM images of the surface microrelief of lead sulfide films within the scanned area (scan area of  $5x5 \ \mu m^2$ ) synthesized at different molar ratios of the initial solution components.

According to AFM data, the surface of the obtained samples is composed of a set of rounded grains with pronounced boundaries, which form complex aggregates (Fig. 4). The average sizes of grains and their aggregates are 205–240 nm and 330–365 nm, respectively (Table 3).



а Fig. 4. AFM images of the surface of the PbS films synthesized at 400°C and C(PbCH<sub>z</sub>(COO)<sub>2</sub>):C(N<sub>2</sub>H<sub>4</sub>CS) ratios of 1:8 (a) and 1:10 (b)

With increasing thiourea concentration in the initial solution, the average  $(R_{a})$  and RMS  $(R_{a})$  roughness, as well as relief height difference ( $\Delta$ ) increase, indicating the formation of films with more prominent surface relief. PbS samples obtained at the same ratios of  $C(Pb(CH_{z}COO)_{2}):C(N_{2}H_{4}CS)$ , at 400 °C, have smoother surfaces compared to films synthesized at 300 °C. Thus, an increase in the deposition temperature leads to the formation of PbS films with a more perfect structure and denser packing of grains. Similar results concerning the effect of temperature on the microstructure of pyrolytic films of lead sulfide were obtained in [26].

1/III

When studying the optical properties of PbS films, we used the power-law dependences

of the absorption coefficient on the photon energy (Fig. 5) to determine the optical band gap (Table 4). The samples obtained at temperatures of 300-400 °C and varying molar ratios of components are characterized by the band gap  $E_{a}$  from 0.41 to 0.45 eV. The obtained results are in good agreement with literature data [9, 15]. The component ratio in the sprayed solution practically does not affect the optical band gap.

µm

h

## 4. Conclusions

Lead sulfide films were synthesized by aerosol pyrolysis of aqueous solutions of "Pb(CH<sub>3</sub>COO)<sub>2</sub> – N<sub>2</sub>H<sub>4</sub>CS" at temperatures of 300 and 400 °C. It was shown that the pH at the beginning of formation

<i>T</i> , °C	$C(Pb(CH_3COO)_2):C(N_2H_4CS)$	Δ, nm	R <sub>a</sub> , nm	R <sub>q</sub> , nm	h, nm	Grain size/ aggregate size, nm
	1:6	569	47	62	370	225 / 340
300	1:8	669	78	97	375	215 / 330
	1:10	717	87	85	375	240 / 365
400	1:8	623	64	81	380	205 / 330
	1:10	673	70	90	375	215 / 350

Table 3. Morphological properties of PbS films

Table 4. Optical band gap (eV) of lead sulfide films

Synthesis temperature,	The ratio of components in the system "Pb(CH <sub>3</sub> COO) <sub>2</sub> – $N_2H_4CS$ "							
°C	1:4	1:6	1:8	1:10				
300	0.43	0.45	0.45	0.45				
400	0.43	0.44	0.41	0.42				





**Fig. 5.** Power-law dependences of the absorption coefficient on the photon energy for PbS films deposited from the "Pb(CH<sub>3</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " solutions: a – at 300 °C, component ratio of 1:6; 6 – at 400 °C, component ratio of 1:10

of lead (II) hydroxo complexes in the solution was 4.5 and their fraction in the solution was 0.03 %. In this case, it is possible to suppress hydrolysis by an excess of thiourea, i.e., by replacing the hydroxo group with N<sub>2</sub>H<sub>4</sub>CS molecules. In order to model the initial solution taking into account the formation of thiourea complexes, we calculated and built three-dimensional diagrams and cross section lines of equal fractions for the  $[Pb(N_2H_4CS)_4]^{2+}$  complex. Thus, we chose the initial concentrations of the components:  $C_{TU} = 5 \cdot 10^{-1} \text{ mol/l}, C_{Pb}^{2+} = 5 \cdot 10^{-4} \text{ mol/l}.$  X-ray phase analysis showed that PbS films

X-ray phase analysis showed that PbS films with cubic structure and preferential orientation (200) were formed from solutions of thiourea complexes of lead. The surface of lead sulfide films was formed by a set of rounded grains with average sizes between 205 and 240 nm, which formed complex aggregates (330–365 nm). We determined that sulfide layers with less dense packing of grains and more prominent surface relief were formed with an increase in the thiourea concentration in the sprayed solution. PbS films deposited at 400 °C had a smoother surface.

Using the data of transmission spectra, we obtained the band gap of PbS for direct transitions

(0.41–0.45 eV). The ratios of the initial solution components have little effect on the optical properties of the deposited layers.

## **Contribution of the authors**

The authors contributed equally to this article.

## **Conflict of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Condensed Matter and Interphases / Конденсированные среды и межфазные границы 2024;26(2): 238-246

E. A. Gannova et al. Deposition of lead sulfide films from "Pb(CH<sub>3</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " aqueous solutions...

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E. A. Gannova et al.

Deposition of lead sulfide films from "Pb(CH<sub>2</sub>COO)<sub>2</sub> –  $N_2H_4CS$ " aqueous solutions...

## Information about the authors

*Elena A. Gannova*, Master of the Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

gannova00@mail.ru

*Margarita V. Grechkina,* Leading Engineer-Physicist of the Center for Collective Use of Scientific Equipment, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-7873-8625 grechkina\_m@mail.ru

*Victor N. Semenov,* Dr. Sci. (Chem.), Professor, Chair of Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-4247-5667 office@chem.vsu.ru *Anatoly N. Lukin*, Cand. Sci. (Phys.-Math.), Leading Engineer-Physicist of the Center for Collective Use of Scientific Equipment, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0001-6521-8009 ckp\_49@mail.ru

*Sergey A. Ivkov*, Cand. Sci. (Phys.-Math.), Lead Electronics Engineer of the Department of Solid State Physics and Nanostructures, Voronezh State University (Voronezh, Russia).

https://orcid.org/0000-0003-1658-5579 ivkov@phys.vsu.ru

*Tatyana V. Samofalova*, Cand. Sci. (Chem.), Associate Professor of the Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-4277-4536 TSamofalova@bk.ru

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