

## Synthesis and Characterization of Chemical Bath Deposited Lead Sulfide Thin Films in Ultrasound and Microwave Irradiation

S.S. TULENIN\*, A.V. POZDIN, K.A. KARPOV, D.A. NOVOTORKINA and M.S. ROGOVOY

Department of Physical and Colloid Chemistry, Ural Federal University, Yekaterinburg, Russia

\*Corresponding author: Tel: + 7 9630311043, E-mail: stast1989@mail.ru

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Lead sulfide thin films were grown by means of chemical bath deposition using thermostatically controlled conditions, microwave and ultrasonic irradiation. The film was characterized by means of XRD, SEM and EDX methods. According to XRD deposited film has a cubic structure of PbS. SEM confirmed nanosize nature of thin film that depend on deposition conditions. The dark resistance and photosensitivity of PbS film is shown to correlate with deposition time, concentration of ammonium iodide in reaction mixture, ultrasound and microwave influences.

**Keywords:** Chemical bath deposition, Lead sulfide, Ultrasound deposition, Microwave irradiation, Dark resistance.

### INTRODUCTION

The thin films of lead chalcogenides have wide application in infrared technique due to their high photosensitivity in the spectral range 0.4-5.0  $\mu\text{m}$  [1-3]. A typical representative of this group is lead sulfide. One of the most effective techniques of quality the lead sulfide films is chemical bath deposition method using thiocarbamide as a source of sulfide ions, ammonium hydroxide, sodium citrate as a complexing agent and different ammonium halogenides as photosensitive additions [3,4]. The PbS thin films have high photosensitivity, that is usually related with the activating effect of the oxygen and halogenide spots into the layer [5]. Also the strong influence on the microstructure and photoelectric properties of the layers are provided their deposition conditions [6].

Ultrasound and microwave irradiation are often used to synthesize novel materials with unusual properties. Ultrasound oscillations can induce the formation of small particles with high surface area. These conditions during ultrasound irradiation are successfully applied to prepare various nanosized materials such as metals, metal carbides, metal oxides and metal chalcogenides [7-9]. The microwave-assisted synthesis is yet another novel method to deposited metal sulfides [9,10]. The application of microwave irradiation result in a change in the degree of ordering of the solvent and the structure of ion solvate shells, deformation of the electron shells of atoms and molecules. It facilitates the interaction of particles, reduce reaction time, increase their efficiency and reaction rates and leads to rapid

volumetric heating [11]. However, in these studies, special attention is paid to obtaining nanoparticles of metal chalcogenides with their possible application, but absolutely not paying attention to photoelectric characteristics of the materials.

In this paper, two novel methods for the preparation of nanocrystalline PbS thin films based on ultrasound and microwave irradiation have been presented. We compared the morphological features and photoelectric characteristics of lead sulfide thin films obtained using thermostatically controlled conditions, ultrasound and microwave irradiation.

### EXPERIMENTAL

Deposition of lead sulfide thin films was carrying out on preliminary defatting sital substrates from reaction mixture containing lead acetate (1 M), thiocarbamide (2 M), ammonium hydroxide, sodium citrate (1.2 M), ammonium iodide (5 M). The lead precursor in the solution gave lead ions. The sodium citrate was used for complexation of lead ions which inhibited reaction of sulfide formation. The ammonium iodide was used as sensitive dopant. A precursor of sulfide ions was thiocarbamide that is unstable in alkaline solution.

Synthesis of thin films was carried out at 80 °C in Mo-glass beaker reactors in which sital substrates fixed in specially made fluoroplastic devices were placed. Reactors were located in water thermostat LOIP LT-116 with the accuracy of maintenance of temperature  $\pm 0.1^\circ$ . Ultrasound deposition was carried out in an ultrasonic bath at 80 °C, a frequency 22.5 kHz and

an irradiation power 30 and 50 W in the reaction solution. Deposition time of such thin films varied from 45 to 90 min. Microwave-assisted heating reactions carried out by using a microwave oven (900 W, 2.45 GHz) at a power 10 %. The microwave oven followed a working cycle of 3 s on and 27 s off. Deposition time in the microwave oven was fixed for all PbS thin films and was 90 min.

Crystal structure of thin films investigated by method of X-ray diffraction (XRD) on diffractometer Shimadzu XRD - 7000 with using monochromatic Cu/K $\alpha$ 1 radiation,  $\lambda = 1.54056$  Å. Shooting led at a room temperature in a scanning mode with step 0.03° and time of accumulation of a signal 20 s.

Scanning electron microscopy (SEM) of a simple surface was occurred on Mira-3-LMY instrument in secondary electron (SE) with JED 2300 tool for energy dispersive X-ray (EDX) analysis. Thickness of samples has been measured on an interferometer MII-4M.

The photoelectric properties of PbS films in the infrared spectral region were studied using a K.54.410 system. The light source used was a  $573 \pm 3$  K blackbody radiator with an irradiation of  $10^{-4}$  W/cm $^2$ . The light modulation frequency and drift voltage were 800 Hz and 50 V, accordingly. The nickel ohmic contacts were electrochemically deposited onto the experimental film samples to perform the photoelectric measurements of semiconductor layers. The square of the sensitive element was 25 mm $^2$ .

## RESULTS AND DISCUSSION

As a result of chemical bath deposition uniform gray films with good adhesion to the sital substrates were obtained. According to the results of interference microscopy measurements, lead sulfide films obtained under thermostatically controlled conditions have the largest thickness up to 500 nm (Fig. 1). It should be noted that the thickness of the layers increases simbatically with increasing synthesis time, which is in good agreement with Maskaeva *et al.* [12]. However, a maximum thickness of PbS layers prepared with an ultrasonic irradiation power of 30 W was only 195 nm and at a microwave-assisted synthesis it was 210 nm, respectively.

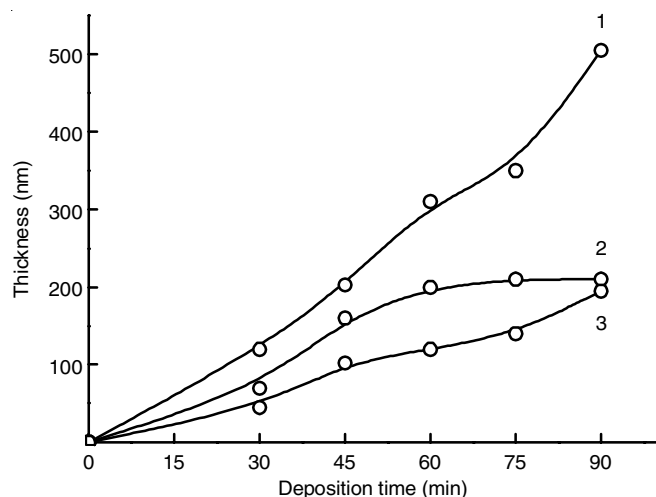


Fig. 1. Thickness of the PbS thin films deposited in thermostatically controlled (1), microwave conditions (2) and ultrasonic irradiation power 30 W and (3) ultrasonic irradiation power 50 W

The X-ray diffraction data (not shown here) showed that independently of the conditions for obtaining films on X-ray diffraction patterns. All diffraction peaks can be indexed as a face-centered cubic structure of PbS with a lattice constant of 5.944 Å (JCPDS card No. 5-0592). But oxygen or iodine containing phases were not detected by X-ray diffraction, because it presented in very small amounts. This is also noted by the previous authors [3,11,12]. The strong and narrow peaks show that the material has good crystallinity and size. EDX-analysis data confirmed the formation of PbS phase without any impurities with a small excess of sulfur at 50.8 % (Table-1).

TABLE-1  
ELEMENTAL COMPOSITION (at. %) OF THE AS-DEPOSITED LEAD SULFIDE FILMS OBTAINED AT 353 K

Deposition condition	Pb	S
Thermostatically controlled	49.2	50.8
Ultrasonic, 30 W	49.6	50.4
Ultrasonic, 50 W	49.8	50.2
Microwave	49.8	50.2

SEM date of the as-deposited PbS films at different deposition conditions are presented on Fig. 2. The study of thermostatically deposited lead sulfide thin films (Fig. 2a) showed that it has a fine-crystalline cubic structure with an average crystal size of 90-400 nm. When ultrasonically acting on the synthesis process (Fig. 2b and 2c), the PbS crystallites lose a pronounced cubic habitus and their agglomeration takes place. The average crystallite size is 200-350 nm. There are large aggregates on a surface that has a size up to 500 nm. The average size of the submicron particles is increased to 150-450 nm with the increase of ultrasonic irradiation power. But the visible shape of the particles is closer to the cubic habitus, which is typical for films obtained in thermostatically controlled conditions. The effect of microwave radiation (Fig. 2d) also contributes to

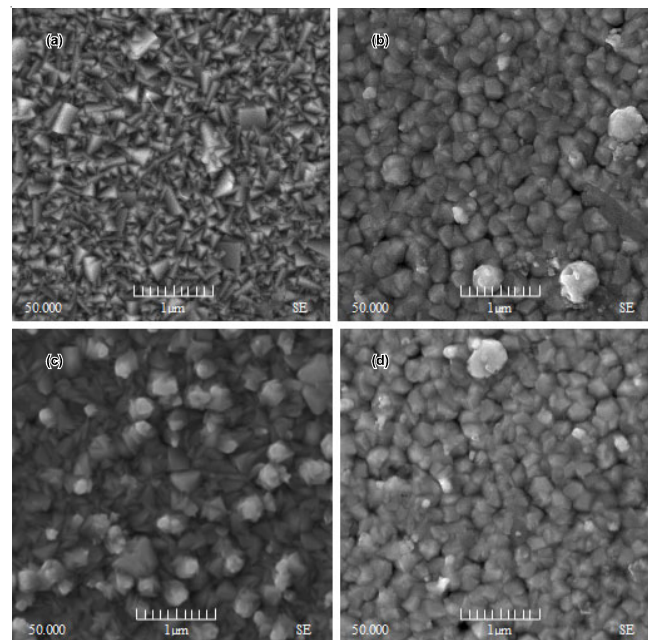


Fig. 2. SEM images of the PbS thin films deposited at thermostatically controlled (a), ultrasonic (b, c) and microwave conditions (d). Power of ultrasonic oscillation were 30 W (b) and 50 W (c); Deposition time 90 min, deposition temperature 80 °C, [NH $_4$ I] = 0.2 mol/L

morphological changes, which leads to a change in the shape of the crystallites and their integration to a size of 150-350 nm. In view of the specific complexity of the synthesis in microwave irradiation most of the particles do not have time to form completely at the end of the deposition process. It negatively affects both the microstructure and the thickness and characteristics of PbS films.

Fig. 3 shows PbS thin films obtained in thermostatically controlled conditions and in microwave irradiation as a function of  $\text{NH}_4\text{I}$  concentration. It can be clearly seen that films obtained in thermostatically controlled conditions have a dark resistance lower by 30 %. It gradually increases with increasing concentration of ammonium iodide in the reaction mixture [5,13]. Probability, such a difference in the dark resistance of the layers is due to their thickness.

The volt-watt photosensitivity for PbS films obtained in thermostatically controlled conditions increases with increasing concentration of ammonium iodide in the reaction mixture (Fig. 3b). This dependence is explained by an increase in the thickness of the layer and in the number of photoactive the oxygen

and halogenide spots [5]. However, such phases were not detected by X-ray diffraction and EDX-analysis, because it was present in very small amounts. The highest photosensitivity is offered by the films sensitized at  $\text{NH}_4\text{I}$  concentration 0.2 mol/L. Their voltage sensitivity is 55  $\mu\text{V}$ . The dependence of volt-watt sensitivity for microwave deposited PbS films is extreme. The highest photosensitivity is offered by this films sensitized at  $\text{NH}_4\text{I}$  concentration 0.15 mol/L. Their voltage sensitivity is 26  $\mu\text{V}$ . We consider the lower sensitivity of PbS layers is related to the rapid microwave heating of volume of the reaction mixture, which leads to uncontrolled formation of thin films and does not contribute to the entry of large concentrations of ammonium iodide as a photoactive additive.

Fig. 4 shows that the PbS thin films obtained in thermostatically controlled conditions and in ultrasound irradiation as a function of the deposition time at constant  $\text{NH}_4\text{I}$  concentration 0.2 mol/L. It can be clearly seen that the deposition time and the thickness of the layers increases, but their dark resistance decreases up to 1000 k $\Omega$ . This dependence is clearly expressed for layers obtained in thermostatically controlled conditions

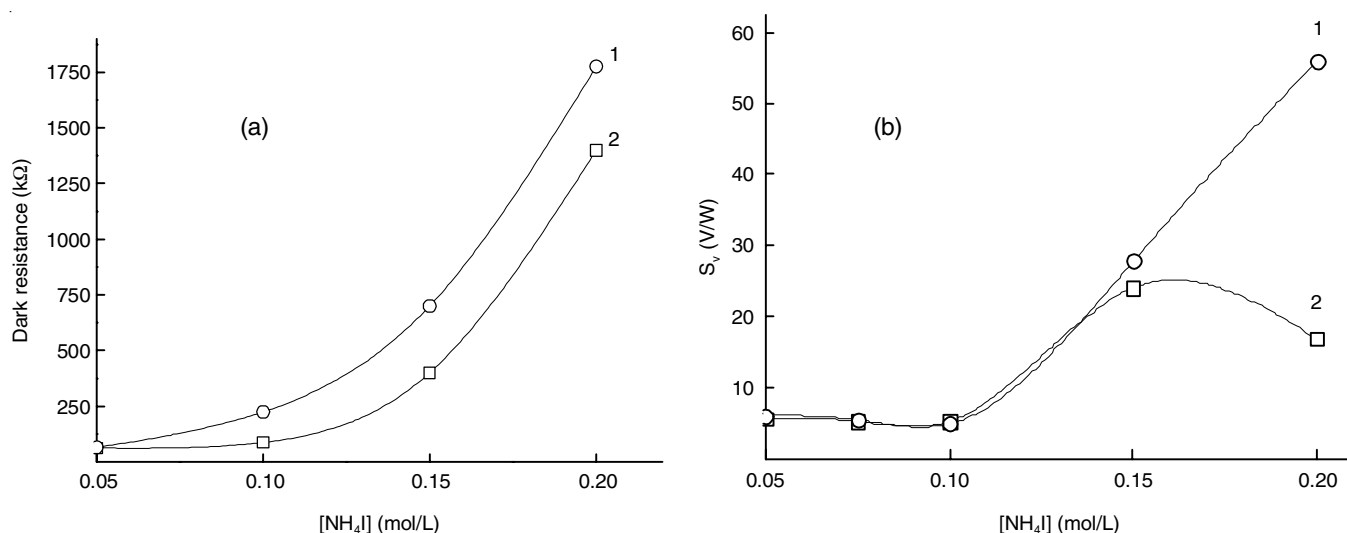


Fig. 3. Dark resistance (a) and volt-watt photosensitive (b) of the PbS thin films deposited in thermostatically controlled (1) and microwave conditions (2)

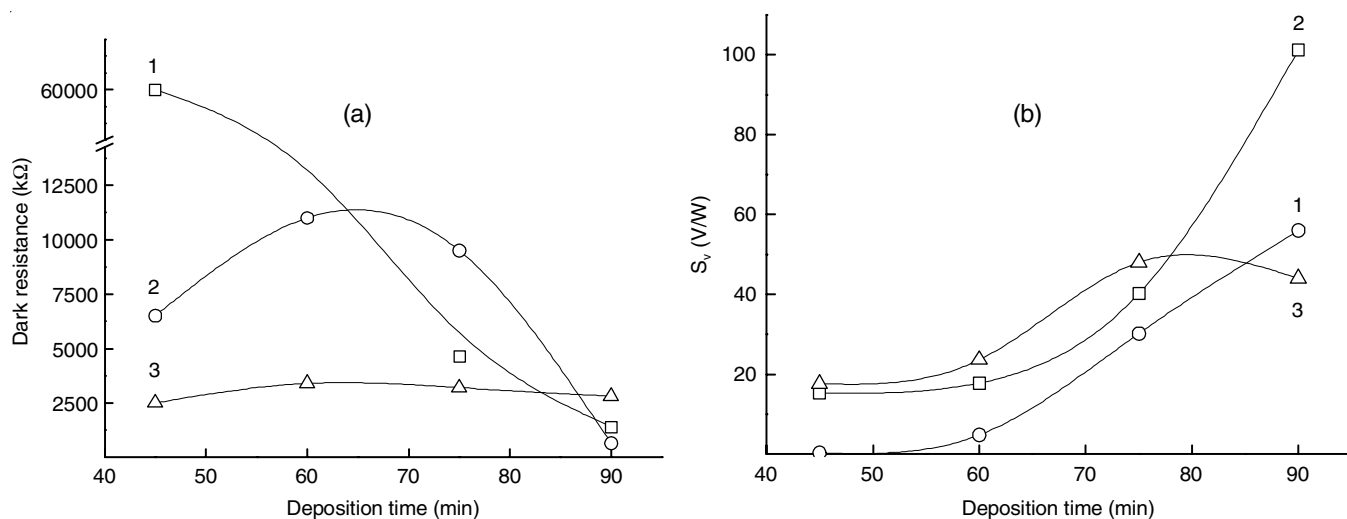


Fig. 4. Dark resistance (a) and volt-watt photosensitive (b) of the PbS thin films deposited in thermostatically controlled conditions (1) and ultrasonic irradiation power 30 W (2) and 50 W (3)

and less for layers in ultrasonic irradiation power of 50 W, whose resistance remained at 2500 k $\Omega$ . The dependence for films obtained by ultrasonic irradiation power of 30 W is extreme with a maximum at 65 min (film thickness is 125 nm).

In comparison with the layers obtained at microwave effect, the dependence of the volt-wattage photosensitivity of ultrasound deposited layers looks more interesting (Fig. 4b). A smooth increase of SV for all obtained PbS films up to 100  $\mu$ V is observed with an increase in the deposition time and with their thickness, accordingly. Exclusion is layers obtained in ultrasound irradiation power of 50 W. However, special attention should be paid to the fact that ultrasonic treatment leads not only to a decrease in the thickness (Fig. 1) and the crystallite size of the layers, but also promotes to a significant increase in the photosensitivity of PbS films at a lower thickness. This is due to the lower crystallinity of the films and accordingly, to a larger surface area capable of receiving active radiation. On the other hand, this is due to the fact that as a result of direct ultrasonic influence on the process of chemical deposition of PbS is effect of acoustic cavitations, *i.e.* the formation, growth and implosive collapse of bubbles created in the liquid. Ultrasound waves that are strong enough to produce cavitations can drive chemical reactions such as oxidation, reduction, dissolution and decomposition [8,9,14]. As a result, ultrasonic treatment increases the reactivity of the substances in the reaction mixture. This promotes to an increase in the occurrence of a photoactivation addition, such as ammonium iodide with long-term maintenance of nanodispersed phase at the initial stage of synthesis, which leads to an increase in the volt-wattage sensitivity. These results indicate the efficiency of chemical bath deposition in ultrasonic irradiation.

## Conclusion

Two novel routes for the deposition of PbS thin films have been established, based on ultrasound and microwave irradiation. Deposited thin films have cubic structure of lead sulfide by means of XRD and EDX analysis. These confirm that thin films has only PbS phase without any impurities with a small excess of sulfur at 50.8 %. Nanosize nature of thin films and modification of their morphology depend on using of ultrasound and microwave irradiations were shown by means of SEM. The dark resistance and volt-watt photosensitivity of PbS films have been measured as functions of NH<sub>4</sub>I concentration and deposition time. It was shown that the voltage

sensitivity of the layers deposited in thermostatically controlled conditions does not exceed 55  $\mu$ V. The sensitivity maximum of the films deposited at microwave and ultrasound irradiations are 26 and 100  $\mu$ V, accordingly. The obtained results showed the direct effect of the microwave and ultrasound deposition conditions of PbS films not only on their surface structure, but also on the main photoelectric parameters. Further studies may extend the chemical bath deposition method for the thin film preparation of other metal sulfides.

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