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The microstructure of the surface of thin PbS films deposited from the coordination compounds diacetatodi(thiourea)lead

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This paper presents the results from a study of the microstructure of the surface of lead sulfide films deposited via the pyrolysis of aqueous $[Pb(N_2H_4CS)_2(CH_3COO)_2]$ aerosols. The influences of temperature and the concentration of thiourea on the synthesized films' surface topography were investigated. A change in the type of conductivity with increasing temperature was observed.

Keywords: method of aerosol pyrolysis, pyrolytic films, coordination compounds, surface microstructure, type of conductivity.

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1. Introduction

Nanoscale objects and systems have a number of specific properties in comparison to their corresponding bulk materials, primarily, this is due to the manifestation of size effects in physico-chemical, optical and electronic properties, allowing an expansion in the range of applications for semiconductors. Additionally, the requirements for surface properties, e.g. roughness of the surface, its purity, uniformity of impurity distribution, etc. over quite large areas are crucial.

The method of scanning probe microscopy is widely used to study a surface with a spatial resolution up to atomic resolution. One of the important modern methods of probe microscopy is atomic force microscopy for the study of microrelief and local surface properties [1].

Along with oxide systems [2, 3], an important place among semiconductor materials with interesting optical, electrical, photoelectric and luminescent properties belongs to metal sulfides and solid solutions based on them. This provides a wide choice of starting materials for the manufacture of infrared detectors, chemical sensors, light-emitting diodes, phototransistors, photopotentiometers, semiconductor lasers [4–6].

A special place among photosensitive materials is occupied by narrow-gap thin layers of lead sulfide, which are widely used in optoelectronics [7].

Traditionally, high-temperature methods of production and vacuum installations which require complex and expensive equipment have been used for the deposition of PbS layers. Therefore, the actual problem is the development of a simple and inexpensive method for spraying solutions of thiourea complexes onto a heated substrate (pulverization method) based on the thermal destruction (pyrolysis) of complex compounds for the synthesis of metal sulfide thin films, thus also permitting the synthesis of materials with controlled properties [8].

Earlier [9–11], we studied lead sulfide films deposited from solutions of $[Pb(N_2H_4CS)_2Cl_2]$ coordination compounds at different temperatures and starting material concentrations.

The purpose of this work is to reveal the relationship between the synthesis conditions and surface properties of lead sulfide films, the deposited layers of di(thiourea) lead(II) acetate, to study the change in the type of conductivity with increasing temperature.

2. Materials and methods

Synthesis of PbS films was carried out by pyrolysis of aerosolized aqueous solutions of thiourea coordination compounds (TCC) $[Pb(N_2H_4CS)_2(CH_3COO)_2]$ formed by the interaction of lead acetate (C^{2+}_{Pb} = 0.1 mol/l) and thiourea (C_{TH} = 0.1–0.5 mol/l). To obtain the samples used, "chemically-pure" grades of $Pb(CH_3COO)_2$ and N_2H_4CS (TH) were used.

The temperature (T) of the sital and quartz substrates was varied from 200 to 450 °C. The deposition time of the PbS film was 2 min.

Investigation of the surface morphology for the obtained samples and the construction of histograms of the distribution of surface heights were performed via atomic force microscopy (AFM) SOLVER P47. The thickness of the obtained films was measured by scanning electron microscopy (SEM) using a Jeol JSM-6510LV instrument. Determination of the conductivity of the samples was done using the hot probe method.

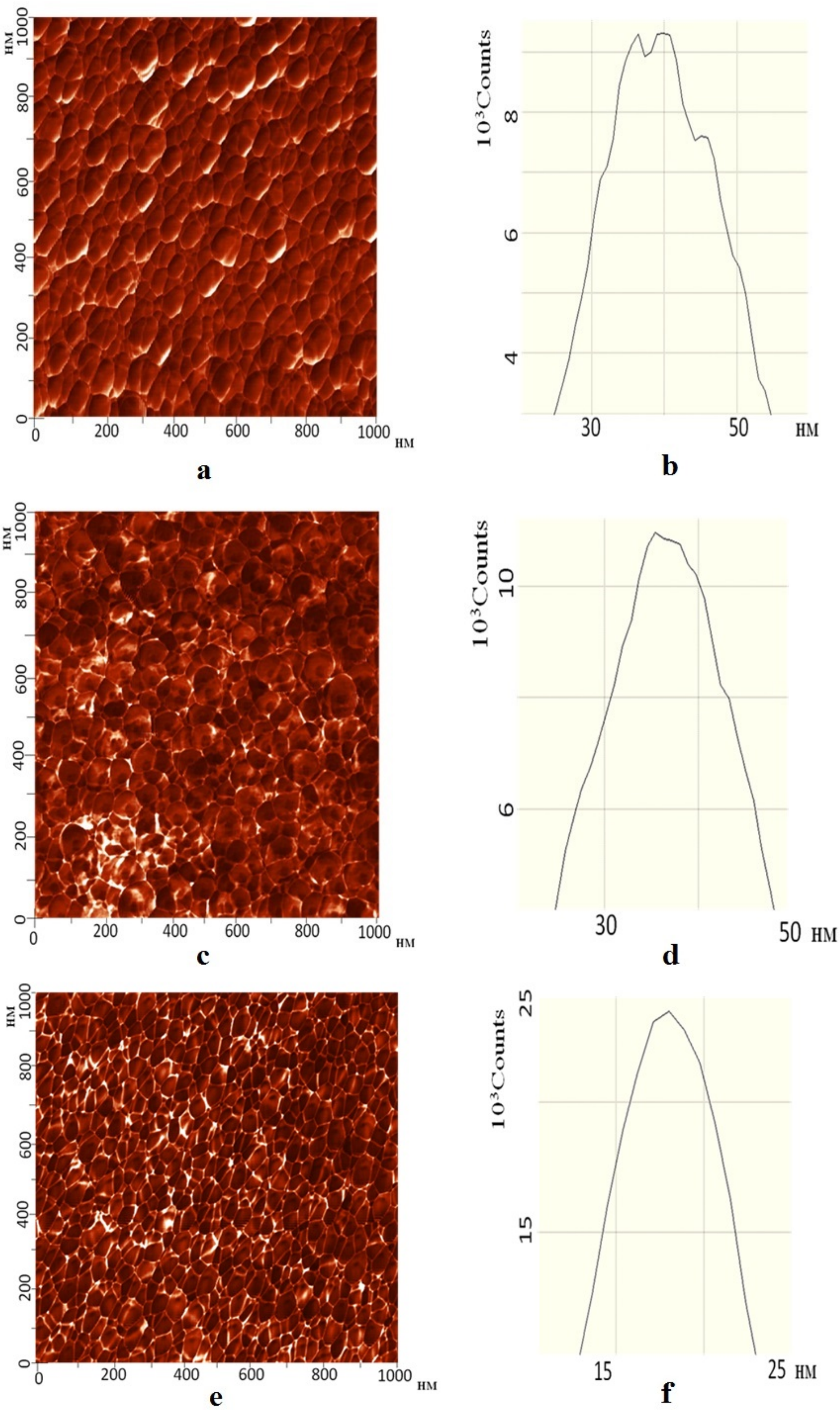

FIG. 1. AFM – surface scans in the phase contrast mode (a, c, e) and a histogram of the distribution density for surface heights (b, d, f) of PbS films synthesized at 200 °C (a, b), 350 °C (c, d) and 450 °C (e, f) (C^{2+}_{Pb} : C_{TH}= 1:2)

3. Results and discussion

Figure 1 shows the surface scans obtained by the method of displaying the phase and the histogram of the density distribution of the surface heights of PbS films precipitated from di(thiourea) lead(II) acetate synthesized at $T = 200$ °C, 350 °C and 450 °C in the ratio of the components of the initial solution of lead acetate and thiourea 1:2. The scanning area was 5×5 μm^2.

The AFM results showed that the microstructure of the surface of the films is formed from round-shaped grains that uniformly cover the surface of the substrate. The average size of the elements is 30–40 nm at temperatures of 200–350 °C and 15–20 nm at 400–450 °C.

From the analysis of microphotographs and parameters, it follows that at low temperatures, the formed grains do not have time to form smoother layers with close grain packing, an increase in temperature from 200 °C to 450 °C leads to the formation of films characterized by a more developed relief and a nanostructured surface.

In the concentration range of the initial components C^{2+}_{Pb}: STM from 1:1 to 1:4, the height difference value within the scanning region (Δ) and the roughness value (Ra) increase, followed by a decrease for 1:5 (Fig. 2, 3). All these data indicate that an increase in the concentration of the sulfur source (TH) leads to the appearance in the solution of unbound thiourea, which interferes with the thermal destruction process and does not participate in the formation of PbS, as a result of which, layers with less developed relief are deposited. The ratio of C^{2+}_{Pb}: C_{TH} 1:2 and 1:3 is the most optimal for obtaining qualitative films according to these parameters.

Analysis of SEM images showed that the surfaces of the synthesized samples are dense and homogeneous, with films synthesized at low temperatures being characterized by a more wavy relief, in comparison to those films obtained at higher temperatures. The thickness of the obtained samples varied from 400–500 nm (Fig. 4).

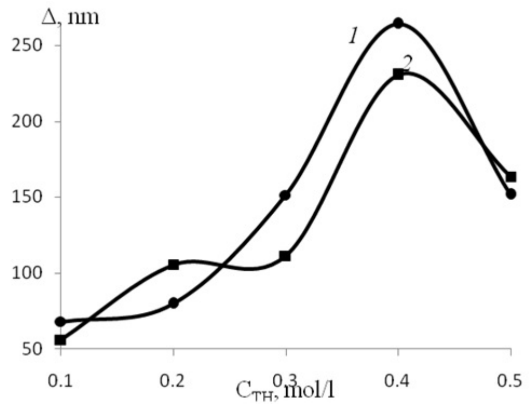

FIG. 2. Dependence of the relief height difference within the scan area at 250 °C (1) and 300 °C (2) on the thiourea concentration in the solution (C_{TH})

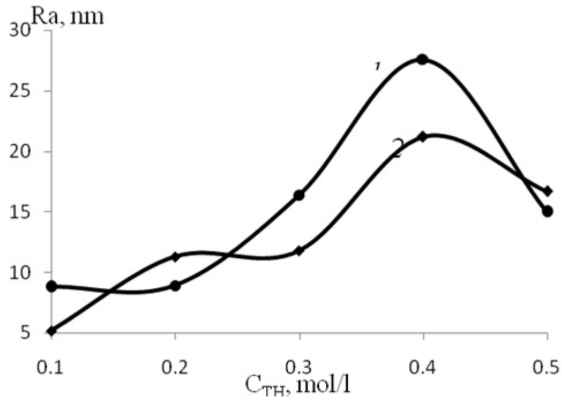

FIG. 3. Dependence of the roughness value at a temperature of 250 °C (1) and 300 °C (2) on the concentration of thiourea in solution (C_{TH})

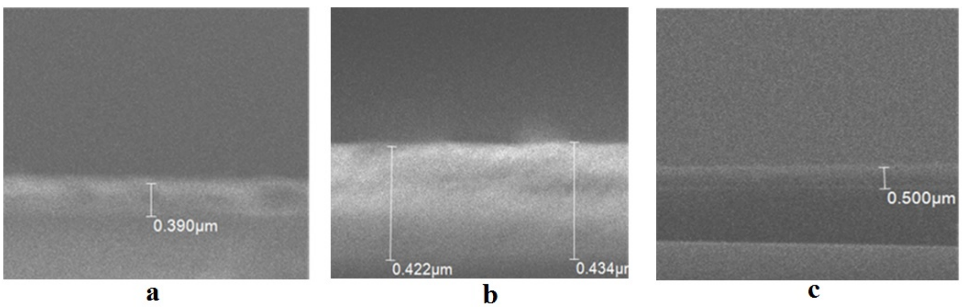

FIG. 4. Electron microscopic images of the surface of PbS films synthesized at a temperature of 250 °C (a = 1:2) and 300 °C (b = 1:1, c = 1:5)

The results of determining the type of conductivity of the samples showed that films obtained at low temperatures up to 300 °C have hole-type conductivity. This can be explained by the fact that under the given conditions, the decomposition of the $[Pb(N_2H_4CS)_2(CH_3COO)_2]$ complex does not take place completely and as a result, fragments of –S–Pb–S– are formed, which creates an excess of sulfur atoms relative to the stoichiometry of the lead sulfide, which Is characteristic of a p-type semiconductor.

With an increase in temperature (350–450 °C), a transition to the electronic type of conductivity occurs, which is due to the fact that the decomposition of the coordination compound occurs more fully, resulting in the formation of –Pb–S– fragments, which participate in lead sulfide formation. At high temperatures, the activity of oxygen increases and it enters the PbS lattice, occupying the sulfur vacancies, and thus, a lack of sulfur ions is created against stoichiometry, which is typical for an n-type semiconductor.

4. Conclusion

The microstructure of the surface of lead sulfide films precipitated from diacetatodi(thiourea)lead at temperatures ranging from 200 to 450 °C was investigated. It is established that as the temperature increases, the film formation was characterized by a more developed relief. With an increase in the concentration of thiourea in the sprayed solution, layers with less developed relief are deposited. In the transition from low to high temperatures, the type of conductivity changes from that of the hole to the electron.

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