The photoluminescence and phase composition of lead sulphide – cadmium sulphide layers obtained by chemical bath deposition

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Abstract. The study concerns optical properties and phase composition studies of the layers based on cadmium sulfide – lead sulfide synthesized by the hydro-chemical deposition. The presence of two peaks in the photoluminescence spectra presumably correspond to two different CdS modifications, i.e. the cubic structure of zinc blende and hexagonal structure (wurtzite type). X-ray phase analysis (XRPA) confirms the presence of both types of crystallites.

1. Introduction
It is known that the layers based on lead chalcogenide and cadmium chalcogenide are traditionally used for creating infrared (IR) photosensitive devices and IR LEDs operating at room temperature [1]. Lead sulfide is a typical representative of AIVBVI compounds class, it is a semiconductor with a band gap of 0.41 eV [2-4]. The crystal PbS has face-centered cubic lattice of the NaCl type. Cadmium sulfide is a representative of AIBVI compounds class. It is a semiconductor with a band gap of 2.42 eV at 300 K. CdS is used in optoelectronics, in both photoreceivers, emitters and solar cells. Cadmium sulfide is crystallized in both the zinc blende (sphalerite) structure and wurtzite structure. Wherein each of the structural modifications can contribute to photoluminescence spectra and determine the optical properties of the created layers.

In this study the aspects of obtaining nanoparticles of lead chalcogenides and solid solutions formed by chemical bath deposition are researched, and its characterization with the use of such methods as X-ray diffraction, photoluminescence measurements is discussed.

1. Experiment
To obtain layers based on lead sulfide – cadmium sulfide the method of chemical deposition from aqueous solutions with the assistance of the following precursors: lead acetate Pb(CH₃COO)₂; sodium citrate Na₃Cit; cadmium chloride CdCl₂ and thiourea (NH₂)₂CS was used. The pH level was adjusted by adding NH₄OH aqueous ammonia solution. The layers were obtained through the technology developed in the Ural Federal University named after the first President of Russia B. N. Yeltsin [5-8].
AFM experiments were performed using NTEGRA-Therma nanolaboratory (NT-MDT, Zelenograd, Russia). Commercial etched silicon tips NSG 01 with typical resonance frequency of 150 kHz were used as AFM probes. Photoluminescence measurements were carried out with spectrometer LabRam HR800 combined with a confocal microscope (manufactured by Jobin-Yvon Horiba). X-ray diffraction experiments were carried out on «DRN Farad» (Cr-Kα).

2. Results and discussion

The samples with different concentration proportions of Pb(CH₃COO)₂ and CdCl₂ in initial solution were obtained on vitroceramic-based substrates, and their properties were examined by analyzing X-ray diffraction data and photoluminescence spectra measurements. The concentration proportions of Pb(CH₃COO)₂ and CdCl₂ in initial solution was 2 (sample 1) and 2.7 (sample 2).

After deposition, the samples were subjected to heat treatment at a temperature T = 200 °C, T = 500 °C, the microstructure was subject to the atomic force microscope investigation. Figure 1 presents AFM images of lateral forces of one of obtained layers before and after annealing.

Figure 1. AFM image of lateral forces of cadmium sulphide – lead sulphide based layer before before heat treatment (a, b), after heat treatment (c). Scan size area is 1 x 1 µm

As it can be seen from figure 1, in some cases crystallites with hexagonal structure were formed. Some crystallites had cubic or pyramidal form.

To determine the phase composition the X-ray phase analysis (XRPA) was used. Fig. 2. shows a bar chart of the layer of the composition 1 before heat treatment. The details of the methods of atomic force microscope investigation and XRPA used are considered in [9, 10].

Figure 2. – Bar chart of cadmium sulphide – lead sulphide based layer before heat treatment
As Figure 2 shows, in the bar chart there are lines that correspond to the PbS and CdS phases. This shows that PbS and CdS layers having a crystalline structure were obtained through the hydrochemical deposition method. It should be specially noted that cadmium sulfide can be seen in two modifications, CdS-wurtzite and CdS-sphalerite. There is also PbO·PbSO\textsubscript{4} complex oxide phase.

It was found that after a low-temperature treatment (T = 200 °C) processing the intensity of the lines corresponding to PbO·PbSO\textsubscript{4} oxysulfate lead increases. No active oxide phases of cadmium in such conditions were recorded.

Figure 3 shows a bar chart of the layer 1 annealed at 500 °C. As Figure 3 shows, cadmium sulfide is still recorded in two modifications, CdS-wurtzite and CdS-sphalerite. There is CdO cadmium oxide phase under the strong temperature influence, and there is also oxysulfate lead. The lines corresponded to CdS – sphalerite are left-shifted in compare to those ones before annealing. There will be no peak corresponding to PbS phase. Thus pointing to its transition to the oxide phase and also a part of lead sulphid goes to solid solution Pb\textsubscript{1-x}Cd\textsubscript{x}S forming.

It should be noted that earlier authors conducted a set of studies on the oxidation effect of polycrystalline layers of lead selenide (and the Pb\textsubscript{1-x}Cd\textsubscript{x}Se solid solutions) on the spectral characteristics of luminescence [11-16]. Despite the variety of technologies for obtaining (thermal spraying and hydrochemical deposition) and replacing selenides with sulfides, the formation of the oxide phases has some common features. At the same time there is a major difference. In fact, the hydrochemical method concerns the coexistence of very limited solid solutions similar in composition to the PbS and CdS phases. Presumably, this is due to lower synthesis temperatures at which the formation of binary solid compounds occurs without the interaction between the PbS and CdS phases to form a solid solution. At higher temperatures, the solubility limit of Pb in CdS rises (especially along the PbS – CdS section).

The photoluminescence spectra were obtained using a spectrometer LabRamHR800 (manufactured by Jobin-YvonHoriba) combined with a confocal microscope. The second harmonic Nd: YAG-laser (wavelength 532 nm) was used as an excitation source. The laser beam is focused to a spot with a diameter of ~1-2 μm on the surface of the sample that allows the measurement of optical properties in different parts of the samples of the inhomogeneous composition. For example, Fig. 4 shows the spectra of the photoluminescence layer of composition 2 before the heat treatment. Lines 1 and 2
correspond to different positions of the laser spot on the sample (No. 1 is the homogenous portion of surface, No. 2 denotes the area corresponding to the exit of individual agglomerates on the surface).

Figure 4 shows that the spectrum obtained with the free surface of the film has a wide loop in the range from 550 to 800 nm.

The spectrum obtained from the nanocrystals is in the same range but it has two distinct maxima near 670 nm and 725 nm. A similar pattern was observed by the authors of the paper [17]. They connect the appearance of two peaks of luminescence with the presence of nanocrystals of two structural modifications of CdS with different bandgap values. Each modification contributes to the optical properties of nanoparticles and leads to the appearance of two luminescence peaks, the first of which can be attributed to the wurtzite structure of CdS, and the second one to CdS nanocrystals of the zinc blende.

It should be noted that the intensity of the photoluminescence spectra obtained from CdS nanocrystals (line 2) is significantly less (by about 5 times) than from the free surface of the film which may be due to multiple reflections of light from the facets of the crystals onto the surface.

Conclusions

With the use of chemical bath deposition method layers based on lead sulfide and cadmium sulfide are obtained, their microstructure, phase composition and luminescence are studied. The atomic force microscopy method revealed that the surface layers before the heat treatment system represent a system of crystallites of the hexagonal and pyramidal shapes. Two peaks are observed on the spectral characteristics of luminescence presumably corresponding to two different CdS modifications, the cubic structure of the zinc blende and the hexagonal structure (wurtzite type). The luminescence
spectra measurement results are well in line with X-ray phase analysis data confirming the creation of CdS crystallites in two different modifications.

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