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Spectral characteristics and morphology of nanostructured Pb–S–O thin films synthesized via two different methods



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ABSTRACT

Using two different experimental techniques, namely chemical vapor deposition (CVD) and physical vapor deposition (PVD), we deposited a lead sulphide (PbS) thin films with a very small lifetime (10^{-9}) . We investigated the morphology of the obtained PbS films using various techniques i.e. AFM, SEM, EDAX, AES and HRTEM. In the case of CVD, we found that the surface consists of grains with dimensions in the plane (diameter to 300 nm and height up to 200 nm), while the same order of the grain size has been observed for PVD. On the other hand, SEM investigation reveals that the PbS particles with various morphologies of both films have uniform and the particle size distribution. Small amount of sodium was obtained from EDXS studies, which may originate from the substrate where the deposition process has been produced at temperature 550-600 °C and for CVD at minimum accelerating voltage 5 kV silicon are presented in the spectrum, which means that the region for X-ray generation voltage data exceeds the thickness of the films (where the thickness of films about 0.4 um). AES confirms the surface laver of these films (PVD) containing carbon and oxygen and it has a thickness of 0.1 µm. At a depth of 1.3 µm in films these elements are again increased, which corresponds to the film thickness of 1.5 µm. Layers of PVD films are seen by HRTEM and the studies confirm that oxygen-layer located on top of the structure, while the layers of CVD films not only have the oxygen along the crystallite boundaries, but also accumulate in the depth of the boundary with the substrate. Our results of morphology indicate that the change in spectral characteristics of films deposited by (CVD and PVD) is related to the structure and the crystalline size.

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1. Introduction

Solar cell technologies are becoming increasingly important in electric power generation. This is due to the fact that they provide more secure power sources and pollution free electric supplies. Semiconductor thin films

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http://dx.doi.org/10.1016/j.mssp.2014.08.010 1369-8001/© 2014 Elsevier Ltd. All rights reserved. are always in focus due to their outstanding electronic and optical properties and possible applications in various devices such as light-emitting diodes [1–4], single electron transistors and field effect transistors [12]. The fabrication of nanocrystalline semiconducting metal chalcogenide has drawn considerable interest in recent years, because of their unusual optical and electric properties and potential applications in nanodevices [6–8]. In recent years, numerous efforts have been made to control the fabrication of nanostructured materials with various morphologies, since the novel properties and potential applications of nanomaterials depend largely on their shapes and sizes [9–11]. The electronic and optical properties of semiconductor materials can be changed by changing their size and shapes [13] as an important IV-VI group semiconductor. PbS is an important direct narrow band gap semiconductor material (\approx 0.41 eV) with a large excitation Bohr radius of 18 nm [14–17]. Furthermore, it has been widely used in many fields such as Pb²⁺ ion-selective sensors [18], IR detector [19], photography [20,21], and solar cell absorption [22-24]. Additionally, due to the non-linear optical properties of the PbS, it presents various applications in optical devices i.e., optical switch [25]. PbS has been utilized as photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings [26,27]. For these applications, we believe that further studies in order to explore the morphology of the PbS films with different particle sizes are required. It has been reported that the particle diameters should vary from a few micrometers for infrared detector applications to several nanometers for quantum dots [28]. However, still intensive research interest in lead chalcogenides and various articles have been reported to explore new parameters in that system [30,29]. Theoretical consideration has been reported by Neustroeva and Osipova in order to further understand the structures of PbS [31,32]. Further properties of PbS layers on a silicon substrate with a sub-layer of SiO₂ have been studied [33]. Although various studies show much attention to the structure, complexity, ambiguity, and manufacture [34], but still lack information from the physics point of view in these systems.

In the respect, this work aims to explain that particular point and more information will be presented. One of the main motivations is to study the photosensitive films made from "Sapphire" because of its distinctive feature which indicated that the films made by the two methods (CVD and PVD). We demonstrate the change in spectral characteristics of films, explain the effect of oxygen on the electronic structure of the energy bands and the morphology of nanostructured films Pb–S–O.

2. Experimental

Photosensitive films from PbS were synthesized by two different methods. First of all, physical method in this method it has been used metal spraying of PbS coating in a vacuum onto heated glass substrates and subsequent heating these films to 550–600 °C at atmospheric air pressure (PVD). Second method is "chemical" methods in this method it has been used PbS layer that has been precipitated from solutions is not subjected to heating above 100–120 °C, but an additional "oxidizing agent," frequently hydrate hydrazine, is added to the solutions (CVD) [35].

The morphology and the crystallography of the Pb–S–O polycrystalline thin films were studied by atomic force microscopy, scanning the surface and energy dispersive microanalysis (EDXS)and high resolution transmission electronmicroscopy (HRTEM).

3. Results and discussion

3.1. Spectral characteristics of Pb–S–O

The spectral characteristics of both PVD and CVD films have been investigated in [36-38]. In the case of PVD (annealing process followed by heating) the spectral characteristics have a peak near the wavelength, $(\lambda) = 2.5 \,\mu\text{m}$ and, corresponding to the bandgap ($E_g=0.4 \text{ eV}$ at room temperature) as shown in (Fig. 1 lower panel). While for CVD films the spectral characteristics have several maximum, which are similar to the structures of the sandwich with different E_g at different (λ) as shown in (Fig. 1 upper panel). From our morphological studies we can outline the difference between them, which may originate, first of all, from the non-optimal film thickness. The thickness of CVD films is about 0.4 um, which is different from the preferred thickness of 1.5 µm but the thickness for PVD films is about 1.5 µm. Secondly, the differences are due to the dissolving of oxygen inside the structure of PbS. It is necessary for dissolving oxygen in all sources, which will be joined with sensitive layers, bonded with electrons and increase the life time of holes where the sensitization process by heat treatment in oxygen atmosphere was used in order to increase the photoconductivity of vacuum evaporated PbS thin films [39]. These holes are represented the majority carriers. However, it should be noted that the effect of oxygen on the electronic structure of the energy bands brings, in particular, a large decrease in the energy band gap under certain conditions.

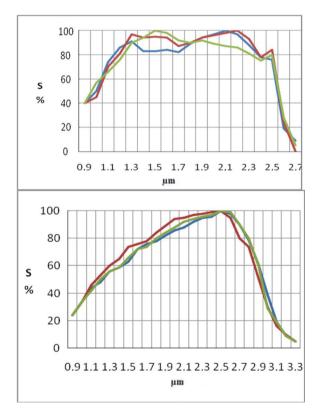


Fig. 1. Spectral characteristics of photosensitive PbS films. (upper panel) Films prepared by CVD and (lower panel) films prepared by PVD.

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