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Structural, optical and electrical characterization of Ag doped lead chalcogenide (PbSe) thin films

A.A. Al-Ghamdi [a],*, S. Al-Heniti [a], Shamshad A. Khan [b]

[a] *Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia*
[b] *Department of Physics, St. Andrew's College, Gorakhpur, UP, India*

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ABSTRACT

Research and development efforts are currently underway to fabricate a variety of solid state devices. A good deal of information regarding the synthesis, structural, optical and electrical properties of Ag doped lead chalcogenides have been revealed. The bulk polycrystalline $(\mathrm{PbSe})_{100-x}\mathrm{Ag}_x$ ternary chalcogenides are prepared by diffusion technique. The XRD patterns recorded for the $(\mathrm{PbSe})_{100-x}\mathrm{Ag}_x$ thin films prepared by vacuum deposition technique, show that these films are polycrystalline in nature. The optical measurements reveal that the $(\mathrm{PbSe})_{100-x}\mathrm{Ag}_x$ thin films possess direct band gap and the band gap energy decreases with an increase of Ag concentration. The extinction coefficient (k) and refractive index (n) are found to be changing by increasing Ag concentration in PbSe. These results are interpreted in terms of the change in concentration of localized states due to the shift in Fermi level. The dc conductivities of $(\mathrm{PbSe})_{100-x}\mathrm{Ag}_x$ thin films are measured in temperature range 303–403 K. It is observed that the dc conductivity increases at all the temperatures with an increase of Ag content in PbSe system. The experimental data suggests that the conduction is due to thermally assisted tunneling of the charge carriers in the localized states near the band edges. The activation energy and optical band gap are found to decrease with increasing Ag concentration in lead chalcogenide and there are good agreements between these two values.

1. Introduction

Lead chalcogenides and their alloys has been the subject of considerable research due to the technological importance of these materials, in crystalline and polycrystalline forms, as detectors of infrared radiation and more recently as infrared emitters and solar control coatings [1–4]. The IV–VI semiconductors are among the most interesting materials in solid-state physics and many of them are found in the rock salt structure. The most widely studied compounds in this group are PbS, PbSe and PbTe. These materials have a narrow band gap, whose temperature coefficient is positive, and they have a high mobility. These lead salts show some interesting optoelectronic applications such as detector devices, light-emitting devices, optical fibers and solar cells. Due to extensive applications and future prospects, lead chalcogenide semiconductors have received much attention in last decades. Thin films of lead chalcogenides plays a crucial role in science and technology due to their wide use in a large number of active and passive devices. Lead chalcogenides are one of the representative types of sensitive membrane materials for the development of conventional chemical sensors selective to metal ions in various liquid media [5–6]. They have been used as sensors for infrared radiation, photoresisters, lasers, solar cells, optoelectronic devices and thermoelectric devices [7–12]. Thermoelectric devices have been used in broad areas such as in consumer products like small refrigerators and in cooling units for fiber junctions in optical fiber communication technology [13–14]. The development of laser technology has opened up new applications for IV–VI compounds. The laser diodes based on lead chalcogenides and their solid solutions are important sources for the tunable radiations in the mid infrared wavelength region. They are considered to be mainly utilized to an advanced measurement system for detecting hydrocarbon pollutants in atmosphere, high resolution spectroscopy and trace gas analysis and also to a new optical fiber communication system over super long distances [15–17].

Among the lead chalcogenides, PbSe is a promising material candidate because of its superior chemical stability and the simplicity of film deposition. The photosensitivity of polycrystalline lead chalcogenide thin films has been the subject of extensive studies [18]. The major advantage of these thin films is the capability to detect a wide range of mid-IR wavelength spectrum (3–5 mm) without the need for cryogenic cooling [19–24]. Polycrystalline PbSe photoconductive detectors (PCD) show nearly constant peak detectivity over the range 77–193 K, comparable to

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* Corresponding author. Tel.: +00966 5056 98959; fax: +00966 269 511.
E-mail address: aghamdi90@hotmail.com (A.A. Al-Ghamdi).

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that at 77 K of similar PCD based on HgCdTe in the respective spectral ranges [20]. At 295 K their detectivity gets notably smaller, but remains high enough to make the PbSe based PCD preferable to detectors based on cooling. By other scores, photovoltaic (PV) devices, e.g. p–n and Schottky junction photodiodes seem mostly advantageous for the IR detection [20]. Their fabrication is possible with: (i) high quality single crystalline film or bulk samples; (ii) polycrystalline films with the grains micron-scale size and a good crystallinity. Polycrystalline semiconductor materials have come under increased scrutiny, because of their potential use in cost reduction of devices for different photovoltaic applications. Ternary lead chalcogenide alloys have many application in photo electrochemical solar cells [25], transistors [26], photoconductors [27], solar control applications [28], etc. They can also be used for the photo- assisted decomposition of water. Obtaining a stable film is one of the prime concerns of any device application of a particular material. Several authors [29–31] has studied the electronic structure calculations of lead chalcogenides, guided mode sand far-field patterns of lead chalcogenide buried hetero structure laser diodes and thermoelectric power and magneto resistance of lead chalcogenide in the region of phase transition.

In the present research work, we have studied the structural, optical and electrical properties of $(PbSe)_{100-x}Ag_x$ thin films. This research work is in continuation of previous research work of the authors [32] in which authors prepared the Cd doped lead chalcogenide (PbSe) and investigates their optical, electrical and structural properties for optoelectronic devices. Now the authors has decided to work on Ag doped lead chalcogenides thin films as they become attractive materials for fundamental research of their structure, properties, and preparation [33–34]. They have many current and potential applications in optics, optoelectronics, chemistry, and biology (optical elements, gratings, memories, microlenses, waveguides, bio and chemical sensors, solid electrolytes, batteries, etc.). [24].

2. Experimental

The bulk ternary $(PbSe)_{100-x}Ag_x$ with $x=3\%$, 6%, 9%, 12% and 15% chalcogenides were prepared by the melt quenching technique. The desired amounts of the constituent elements (99.999% purity) were weighed according to their atomic percentage and then sealed in quartz ampoules under a vacuum of 10^{-6} Torr. The bulk samples of $(PbSe)_{100-x}Ag_x$ was prepared in two steps. Firstly, we have prepared PbSe in polycrystalline form and then $(PbSe)_{100-x}Ag_x$ in polycrystalline form. The sealed ampoules containing the samples PbSe and Ag were kept inside a programmable furnace, where the temperature was raise up to 1000 °C at a rate of 4 °C per min and then maintained it for 14 h. During the melt process, the ampoules were agitated frequently in order to inter mix the constituents to ensure homogenization of the melt. The ampoules having the material in molten state were allowed to cool down to room temperature. The ingots of the sample were taken out by breaking the ampoules.

Thin films of $(PbSe)_{100-x}Ag_x$ with thickness 3000 Å were prepared by using an Edward Coating Unit E-306, onto glass substrates at room temperature on the base pressure of 10^{-6} Torr using a molybdenum boat for optical measurements. The thickness of the films was measured by using a quartz crystal monitor (Edward model FTM 7). The earthed face of the crystal monitor was facing the source and was placed at the same height as the substrate. The evaporation was controlled by using the same FTM 7 quartz crystal monitor. A JASCO, V-500, UV/VIS/NIR computerized spectrophotometer with photometric accuracy of ± 0.004 in absorbance and $\pm 0.3\%$ in reflectance measurements was used for measuring optical absorbance and reflectance in the wavelength region 400–1400 nm.

For dc conductivity, well-degassed corning glass substrates, having pre-deposited indium electrodes (two thick indium electrode) were used as a substrate for deposited amorphous films in the planer geometry. All films were prepared by evaporation technique keeping substrate at room temperature at a base pressure of about 10^{-6} Torr. The thickness of the films was ≈ 5000 Å. The deposition parameters were kept almost the same for all the samples so that a comparison of results could be made for various samples.

For dc conductivity measurement, a constant dc voltage is applied across the sample and the resulting current at different temperature was measured by Keithley-6517 A electrometer. The temperature of the film was increased from 303–403 K by a step value of 5 K. All the measurements were performed under a vacuum furnace Neytec Qex, where a vacuum of about 10^{-3} Torr was maintained throughout the measurements.

3. Results and discussions

The X-ray diffraction patterns of $(PbSe)_{100-x}Ag_x$ chalcogenides thin films were recorded by using X-ray diffractometer model X'per PANalytical supplied with a copper target ($\lambda Cuk_{\alpha 1}=1.5406$ Å), Nickel filter, crystal monochromator was used to examine the crystal structure of the $(PbSe)_{100-x}Ag_x$ thin films. The working conditions were 40 kV, 30 mA, step zie 0.05°, measuring time 2.5 s per step and two theta range from 20 to 100 degrees. The X-ray diffraction traces were taken at room temperature, shown in Fig. 1(a–d). The presence of sharp structural peaks in the XRD spectra reveals that the films are polycrystalline in nature. XRD spectra of $(PbSe)_{100-x}Ag_x$ chalcogenides thin films show the peaks of PbSe, Ag_2Se and Se. It is understood from this spectra that some of the atomic percentage of Ag is reacted with selenium and thereby forming Ag_2Se compound. The observed peaks corresponding to the (111), (200), (220), (311), (222), (400), (331), (420), (422), (511), (440), (531) and (442) are planes of PbSe phase, whereas (111), (102), (120), (112) and (121) planes belong to Ag_2Se phase and (100), (102) (111), (210) planes of Se phase. The films of $(PbSe)_{100-x}Ag_x$ exhibit prominent and intense diffraction peaks at 29.13°, which correspond to the (200) plane of PbSe indicating the predominant growth of crystallites in this direction. Lead selenide (PbSe) has cubic crystal structure with lattice constant 6.1280 Å, space group Fm-3m [42]. Selenium (Se) has hexagonal crystal structure with lattice constants $a=4.3662$ Å, $c=4.9535$ Å and space group P3121 [43], Silver selenide (Ag_2Se) has orthorhombic crystal structure with lattice constants $a=4.3330$ Å, $b=7.0620$ Å, $c=7.7640$ Å and space group P212121 [44].

The experimental d-values for $(PbSe)_{100-x}Ag_x$ thin films were calculated from the Bragg's relation, $2d_{hkl}\sin\theta_{hkl}= n\lambda$ (in our case $n= 1$, $\lambda= 1.5406$ Å) by taking 2θ values from the peaks of X-ray diffraction patterns, are listed in Table 1. The observed interplaner distance "d" values of PbSe, CdSe, (Ag_2Se) and Cd (Se) were compared with standard JCPDS "d" values [35–37]. The d-values are in good agreement with those of the standard values (see Table 1). The last column in Table-1 shows the difference $\Delta d(\text{Å})= d(\text{Å})_{JCPD}-d(\text{Å})_{Exp}$. In the present system, it is suggested that the overall alloy of $(PbSe)_{100-x}Ag_x$ shows a polycrystalline nature.

The optical absorption and reflection spectra of polycrystalline $(PbSe)_{100-x}Ag_x$ thin films grown by thermal evaporation were recorded at room temperature in the wavelength range of 400–1400 nm. The electronic transition between the valance and conduction bands starts at absorption edge corresponding to the minimum energy difference between the lowest energy of the conduction band and the highest energy of the valence band in crystalline materials. The fundamental absorption edge in most