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Optoelectronic and thermoelectric properties in Ga doped β- PbS_2 nanostructured thin films

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ABSTRACT

Lead sulphide nanostructured thin films were grown on soda lime glass substrates by chemical bath deposition. The films were then doped with gallium using vacuum evaporation technique. X-ray diffraction (XRD) established the structural type of the host films to be tetragonal β-PbS_2 with average grain size of the order of 15 nm. The nanostructure of films was further confirmed from scanning electron and atomic force micrographs. The shift in the binding energies of the 4f and 4d states of lead, 2p state of sulphur and the 2p states of Ga from their elemental binding energy values, determined from X-ray photoelectron spectroscopy (XPS), indicated intact chemical bonding in the compound. Compositional analysis showed about 0.01% doping of Ga into PbS_2. Low temperature thermopower measurements indicated *p*-type conductivity for the films with Fermi level positioned at about 0.017 eV above the maxima of valence band. Optical absorption studies in conjunction with photo sensitivity measurements established its pertinence in junction formation in photovoltaic applications due to the blue shift in the band gap to 2.37 eV and the increased photoconductivity of the films.

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1. Introduction

The IV–VI family lead sulphide is a widely studied compound due to its extensive applications in diode lasers, optical detectors, optoelectronic devices, photoresistors, sensors etc. [1–3]. But a search of literature evinced that very few studies are done on the tetragonal β-PbS_2 and no studies are found to be reported on nanostructured thin films of β-PbS_2 doped with gallium. The doping has been tried by different investigators to improve the performance of PbS in optoelectronic devices [4,5]. Doping PbS with bismuth is reported to produce a blue shift in band gap [5].

In this paper, we report the results of an initiating study on the effect of Ga doping on the optoelectronic and thermoelectric properties of β-PbS_2 thin films. Ga is doped by vacuum evaporation in the nanostructured β-PbS_2 thin films deposited by chemical bath deposition and structurally, compositionally and morphologically characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2. Experimental techniques

The host thin films of β-PbS_2 were deposited at room temperature on thoroughly cleaned soda lime glass substrates dipped vertically (for 1 h) in a chemical bath of 1 M lead acetate, 1 M thiourea and predetermined quantity of triethanol amine and ammonia solution taken in a beaker. The pH of the solution was maintained at 9 by controlling the quantity of ammonia throughout the time of deposition. Ga was doped into selected samples of β-PbS_2 by thermal evaporation in vacuum (pressure of 10^{-6} Torr) keeping the deposition temperature at 523 K. The temperature of the doped samples was then raised to about 623 K to ensure the incorporation of Ga into the host film and for the stabilization of the compound. A Rigaku D Max C X-ray diffractometer with CuKα1 (1.54 Å) as source radiation was used to obtain the XRD data on doped and as-prepared thin films. An ESCA machine of VSW

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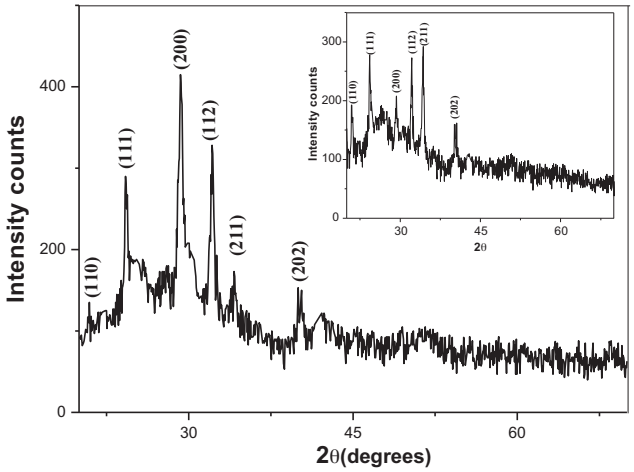

Fig. 1. XRD pattern of a typical Ga doped β-PbS_2. Inset shows the XRD pattern on the host film β-PbS_2.

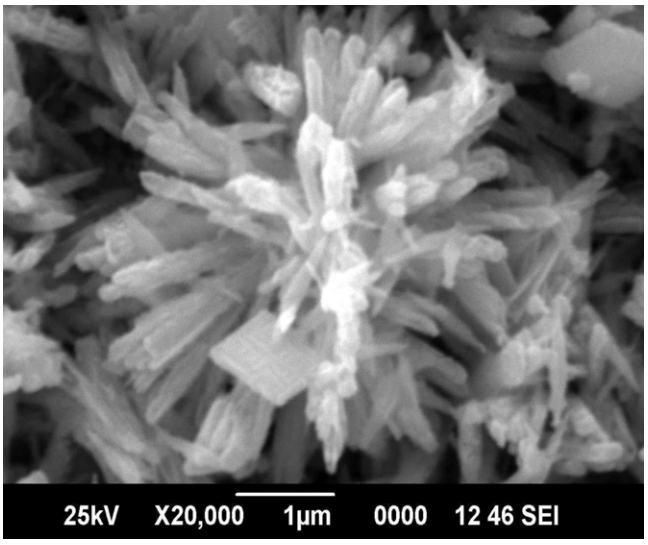

Fig. 2. SEM of a typical doped β-PbS_2 thin film.

scientific instruments make with Mg and Al twin anode X-ray source has been used for recording the XPS spectra of the samples. A 'Collect W' software was employed for recording the XPS data with C-1s peak as the standard for the calibration of the photoelectron spectrometer. For morphological studies, an AFM nanoscope E, Digital Instruments with a silicon nitride cantilever was employed to probe different portions of the film surface in "contact AFM mode". A Cambridge instrument Model no: S-360 machine has been used for taking the scanning electron micrographs. The optical absorbance was measured using a Hitachi U-3410 UV–vis-NIR spectrophotometer. Thermopower measurements of the samples (0.5 cm × 0.2 cm) were performed by placing it between two oxygen free highly conducting (OFHC) copper blocks after applying silver paste for ohmic contact at the ends, so that the junctions were formed at the two ends of the sample. A temperature controller was used to maintain the temperature difference T between the two OFHC blocks using the chromel-Au–Fe (0.07%) thermocouple and a heater wire wound on the lower OFHC block. A nanovoltmeter coupled through a nanovolt scanner card was used to measure the V and the T via the chromel-Au–Fe (0.07%) thermocouple. The sample holder was attached to a heat sink with a removable cylindrical OFHC jacket serving as a radiation shield. The sample holder with wiring assembly was loaded in the cryostat. The TEP data S_{meas} was recorded through a personal computer for a desired temperature step and range. The Seebeck coefficient of the copper reference S_{Cu} was subtracted from the measured S_{meas} such that the sample S was obtained as $S = S_{meas} - S_{Cu}$ [6]. Seebeck coefficient measurements on the samples were done in the low temperature range 80 K to 300 K using liquid nitrogen as the coolant.

Conductivity at room temperature was measured using Keithley 2611A source meter applying silver paste as the ohmic contact. The photosensitivity was measured using the Keithley 2611A after illuminating the samples using an FSH lamp (82 V, 300 W).

3. Result and discussion

The accountable peaks in the XRD pattern corresponded to reflections from (1 1 0), (1 1 1), (2 0 0), (1 1 2), (2 1 1) and (2 0 2) [JCPDS file no: 20-0596] in both the as prepared and doped β-PbS_2, with some modification in the intensity of the peaks when the dopant was added (Fig. 1). From the XRD data, the grain size of the lead sulphide particles were determined to be ~15 nm using Scherrer's formula [2,7,8] which indicated the formation of nanostructured films.

Scanning electron micrographs (Fig. 2) indicated flower like growth of the nanostructured film on the substrate surface, where nanograins of average size around 18 nm agglomerated to form petal like structures of flower. Atomic force micrographs (Fig. 3) corroborated the observation from SEM ascertaining the self-assembling of nanograins in the film.

XPS measurements (Fig. 4) were done to check whether doped gallium formed chemical bonds with the host compound or were just dispersed in the film in the elemental state. The shift in binding energy of Ga 2p3/2 peak from the elemental peak position 1117–1119 eV confirmed the chemical bonding of the dopant with the host β-PbS_2. In the same way, the binding energy positions of 4f and 4d states of lead and 2p state of sulphur (Fig. 4, Inset) affirmed intact chemical bonding between the anions and cations in the film. The compositional analysis, considering the atomic sensitivity factors and areas of different peaks for each element from the detailed XPS spectrum indicated a slight reduction in atomic % of S when Ga doped films were annealed from 623 K, the change being from Pb:S = 1:2 in the host films to ~1:1.9 in the doped films. This might be because sulphur ions escaped from the film surface while the temperature of the films was increased. Measurements were taken on films doped with ~0.01% of Ga.

Optical absorbance versus wavelength curve depicted in Fig. 5 showed a shift of the fundamental absorption edge to higher frequency side in Ga doped β-PbS_2 when compared to that in undoped β-PbS_2. Absorption coefficient (α) calculated from the absorbance

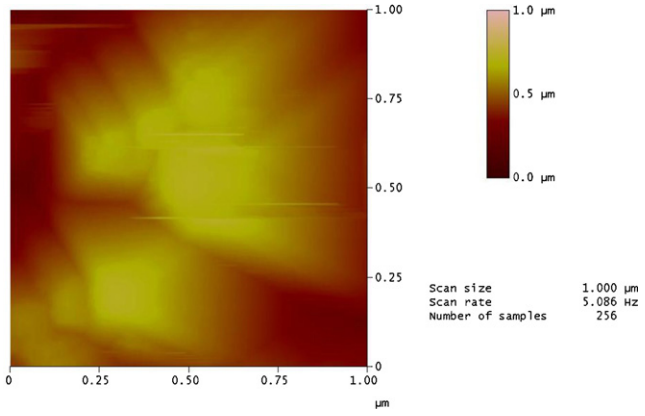

Fig. 3. AFM of Ga doped β-PbS_2 thin film.

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