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Effect of doping concentration on the properties of bismuth doped tin sulfide thin films prepared by spray pyrolysis

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ABSTRACT

Bismuth doped tin sulfide (SnS:Bi) thin films were deposited onto glass substrates by the spray pyrolysis technique at the substrate temperature of 350 °C. The effect of doping concentration [Bi/Sn] on their structural, optical and electrical properties was investigated as a function of bismuth doping between 0 and 8 at%. The XRD results showed that the films were polycrystalline SnS with orthorhombic structure and the crystallites in the films were oriented along (111) direction. Atomic force microscopy revealed that the particle size and surface roughness of the films increased due to Bi-doping. Optical analysis exhibited the band gap value of 1.40 eV for SnS:Bi (6 at%) which was lower than the band gap value for 0 at% of Bi (1.60 eV). The film has low resistivity of 4.788×10^{-1} Ω-cm and higher carrier concentration of 3.625×10^{18} cm^{-3} was obtained at a doping ratio of 6 at%.

1. Introduction

Tin sulfide (SnS) is a IV–VI group of semiconducting material with orthorhombic structure. It has potential use in solar cell for absorber material, due to its high absorption coefficient ($\alpha > 10^4$ cm^{-1}) [1] and high conversion efficiency of about 25% [2]. In addition, the constituent elements are non-toxic and abundant in nature compared to CdTe and $CuInSe_2$ (CIS).

Many techniques have been used to deposit SnS thin films such as vacuum evaporation [3], rf-sputtering [4], chemical bath deposition [5], spray pyrolysis [6], dip deposition [7], etc. Among these methods, the spray pyrolysis is a simple and cost-effective technique for producing large area deposition.

Doping of SnS thin films with In [8], Sb [9], Bi [10], Cu [11], and Ag [12] has been reported to improve their electrical and optical properties. Among these dopant materials, the properties of bismuth doped tin sulfide thin films have not been studied clearly, though it is one of the most promising candidates in the fabrication of SnS based absorber materials [10,13]. Hence, we have tried to prepare Bi-doped SnS thin films by using the spray pyrolysis technique. In the present work, the effects of Bi-doping on the structural, optical and electrical properties of SnS thin films have been reported.

2. Experimental details

Bismuth doped tin sulfide thin films (SnS:Bi) were deposited onto 75×25 mm^2 microscopic glass substrates by the spray pyrolysis technique. The precursors of $SnCl_2 \cdot 2H_2O$ (0.1 M) and thiourea (0.1 M) were dissolved separately in a solution containing deionized water and isopropyl alcohol in proper ratio. Equal volumes of these two solutions were mixed together and sprayed onto the glass substrates at the substrate temperature of 350 °C. Bismuth was doped with SnS thin films using $BiCl_3$ ([Bi/Sn] = 0–8 at%) as the dopant source. The substrates were first cleaned in a water bath, followed by

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dipping in conc. HCl, acetone and ethanol successively. Finally the substrates were rinsed in deionised water and allowed to dry in a hot air oven. In spray unit, the substrate temperature was maintained with the help of a heater, controlled by a feedback circuit. During spray, the substrate temperature was kept constant with an accuracy of 5 K. Spray head and the substrate heater were kept inside a chamber, provided with an exhaust fan for removing gaseous by-products and vapors from the solvent. The spray head was allowed to move in the *X–Y* plane using the microcontroller stepper motor, in order to achieve a uniform coating on the substrate. The spray head could scan an area of 200×200 mm^2 with *X*-movement at a speed of 20 mm/s and *Y*-movement in steps of 5 mm/s simultaneously. In the spray unit, there was a provision for controlling the spray rate of the solution as well as the presence of carrier gas. The microcontroller device was communicated with PC through the serial port in which the data of each spray could be stored. The values of deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept at 3 ml/min, 1.0 kg/cm^2 and 20 cm, respectively. After deposition, the film was allowed to cool slowly to room temperature and washed with distilled water and then dried.

The structural characterization of the deposited films was carried out by the X-ray powder diffraction technique using a JEOL JDX-803 diffractometer (monochromatic CuKα radiation, $\lambda = 1.5406$ Å). Film thickness was measured by the Stylus Profilometer (Mitutoyo SJ 301). The surface topography of the films has been studied by Atomic Force Microscopy (AFM) using the Nano-Surf Easy Scan2. Optical measurements were carried out using a Varian-Cary 500 scan UV–vis–NIR double-beam spectrophotometer in the wavelength range of 400–1200 nm. The electrical resistivity, carrier concentration and mobility were measured by automated Hall Effect measurement (ECOPIA HMS-3000) at room temperature in a van der Pauw (VDP) four-point probe configuration. A schematic diagram of a rectangular van der Pauw configuration is shown in Fig. 1.

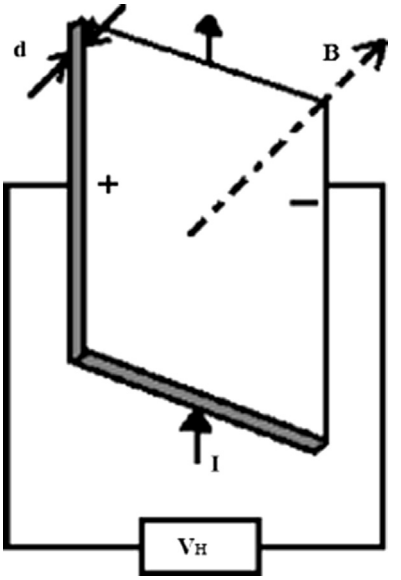

Fig. 1. Sample geometry used for the Hall Effect measurement.

3. Results and discussion

3.1. Structural properties

Fig. 2 showed the XRD pattern of bismuth doped tin sulfide thin films deposited at different bismuth doping ratios at the substrate temperature of $T_s = 350$ °C. All the films were polycrystalline in nature with orthorhombic crystal structure of preferred grain orientation along (111) plane. No extra peaks could be detected while doping related to bismuth, and their sulfide and other compounds. The observed peak position values were compared with the standard data (JCPDS 39-0354). As shown in Fig. 2, with increasing doping concentration, the peak intensities become more intense and sharper at the doping ratio of 6 at% indicating a good crystallinity and decreased progressively as the doping concentration increased above >6 at%. The decrease in the intensity of (111) peak may indicate an increase of stacking defects and loss of periodicity in the SnS lattice arrangement. An increase in peak position of (111) plane with increasing doping concentration attributed the shift from its normal value which represented the

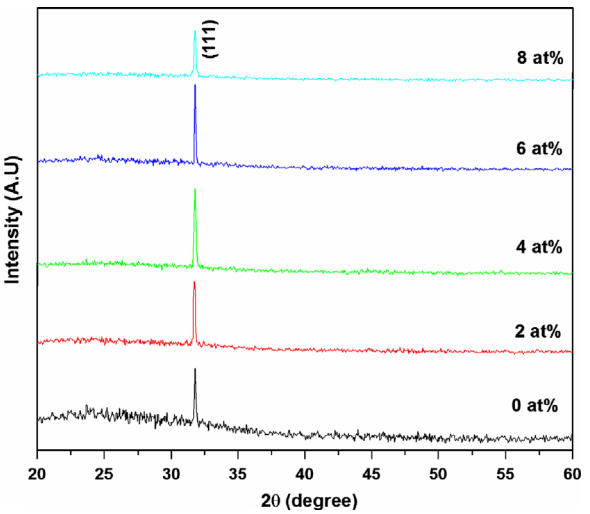

Fig. 2. XRD pattern of films prepared at different ratios of bismuth doping for SnS:Bi thin films.

residual stress in the film caused by the difference in ionic size between Sn^{2+} (0.93 Å) and Bi^{5+} (0.74 Å). This is confirmed by lattice parameters, *a–c*, which were less than the standard value which was strong indication of stress in the films. Guo et al. [9] also observed the shift of (111) diffraction peak with increase in doping concentration.

The average size of the crystallite was estimated by Scherrer's formula

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where $K = 0.89$ is the shape factor, λ is the X-ray wavelength of CuKα radiation, θ is the Bragg angle and β is the full width at half maximum of the peak. The micro-strain