Materials Science in Semiconductor Processing 48 (2016) 39–44

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Effect of substrate temperature on structural, morphological, optical and electrical properties of $MnIn_2S_4$ thin films prepared by nebulizer spray pyrolysis technique

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ARTICLE INFO

Available online 16 March 2016

Keywords:
$MnIn_2S_4$ thin films
Spray pyrolysis
Structural properties
Optical properties
Electrical properties

ABSTRACT

Manganese indium sulphide ($MnIn_2S_4$) thin films were deposited using an aqueous solution of $MnCl_2$, $InCl_3$ and $(NH_2)_2CS$ in the molar ratio 1:2:4 by simple chemical spray pyrolysis technique. The thin film substrates were annealed in the temperature range between 250 and 350 °C to study their various physical properties. The structural properties as studied by X-ray diffraction showed that $MnIn_2S_4$ thin films have cubic spinel structure. The formation of cube and needle shaped grains was clearly observed from FE-SEM analysis. The energy dispersive spectrum (EDS) predicts the presence of Mn, In and S in the synthesized thin film. From the optical studies, it is analyzed that the maximum absorption co-efficient is in the order between 10^4 and 10^5 cm^{-1} and the maximum transmittance (75%) was noted in the visible and infrared regions. It is noted that, the band gap energy decreases (from 3.20 to 2.77 eV) with an increase of substrate temperature (from 250 to 350 °C). The observations from photoluminescence studies confirm the emission of blue, green, yellow and red bands which corresponds to the wavelength range 370–680 nm. Moreover, from the electrical studies, it is observed that, as the substrate temperature increases the conductivity also increases in the range $0.29\text{–}0.41 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$. This confirms the highly semiconducting nature of the film. The thickness of the films was also measured and the values ranged between 537 nm (250 °C) to 483 nm (350 °C). This indicates that, as the substrate temperature increases, the thickness of the film decreases. From the present study, it is reported that the $MnIn_2S_4$ thin films are polycrystalline in nature and can be used as a suitable ternary semiconductor material for photovoltaic applications.

1. Introduction

$MnIn_2S_4$ is a ternary magnetic semiconductor that has a cubic spinel structure [1]. $MnIn_2S_4$ is formed by both direct and indirect transitions [2] and that finds applications in the fields of optoelectronic and functional devices [3–5]. This becomes possible due to the stability and wide band gap (2.0–3.7 eV) of indium sulphide [6]. Moreover, indium sulphide can act as a suitable and effective compound for replacing cadmium sulphide (CdS) in the making of solar cells [7–9]. For compounds such as $MnIn_2S_4$, indium sulphide can be used as a suitable binary base material [10]. There are various methods in which $MnIn_2S_4$ thin films can be grown, like that of the spray pyrolysis, chemical bath deposition, thermal evaporation, atomic layer chemical vapour deposition, sol-gel and reactive sputtering methods [11–16] Out of these, the spray pyrolysis method is a simple, eco-friendly method that consumes very less time for deposition on a substrate with minimum wastage of the base material [17,18]. It is a well known fact that the method of deposition, the various factors governing the process of deposition, the thickness of the film could greatly vary the physical property of the deposited thin films [9].

Information on structural and optical properties for the $MnIn_2S_4$ thin film was provided by Sharma et al. 2005 [1], but studies relating to electrical properties were not carried widely by researchers [7,19]. The current paper aims to discuss on surface morphology, chemical composition and electrical properties along with structural and optical properties of $MnIn_2S_4$ thin film at various substrate temperatures maintained at a constant spray time. The primary objective of this study is to grow a highly transparent thin film by spray pyrolysis method and to obtain maximum transmittance and electrical conductivity, which could find wide application in the field of semiconductor devices.

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http://dx.doi.org/10.1016/j.mssp.2016.03.008
1369-8001/

2. Materials and methods

2.1. Material deposition

The $MnIn_2S_4$ thin films were prepared by a simple spray pyrolysis technique on a glass substrate using the aqueous solution of $MnCl_2$, $InCl_3$ and $(NH_2)_2CS$ in the molar ratio 1:2:4. Here, compressed air was used as the carrier gas. The glass substrate was heated at various temperatures between 250 and 350 °C, and the prepared aqueous solutions were sprayed on the heated substrate in the air medium at a spray rate of 2 mL/min. The chemicals used in the present study were of analytical grade.

The following reaction mechanism takes place in the formation of $MnIn_2S_4$ thin films and the reactions are as follows:

$$MnCl_2 + (NH_2)_2CS + 2H_2O \rightarrow MnS + CO_2 + 2NH_4Cl \quad (1)$$

$$2InCl_3 + 3(NH_2)_2CS + 6H_2O \rightarrow In_2S_3 + 3CO_2 + 6NH_4Cl \quad (2)$$

Since, the products like NH_4Cl, and S are volatile at reaction temperature, the two binary compounds (MnS and In_2S_3) in the reactions (1) and (2) combines to form $MnIn_2S_4$, which is a ternary compound. The reaction is given below:

$$MnS + In_2S_3 \rightarrow MnIn_2S_4 \quad (3)$$

2.2. Characterization techniques

X-ray diffraction patterns of $MnIn_2S_4$ thin films were recorded using X' pert PRO Analytical- PW 1710 with CuKα radiation having wavelength 1.5406 Å operated at 40 kV and 30 mA. The 2θ angle of the detector was scanned from 10° to 80° with a step size of 0.05°. The surface morphology of the thin films was examined by using FEI Quanta-250 Field Emission Scanning Electron Microscopy (FESEM) operated at 30 kV with a scanning rate of 50 µs. The elemental compositional analysis was carried out using an energy dispersive X-ray Spectroscopy (EDS- model: JOEL-JEM 2100). Optical properties of the films were measured using an UV–vis spectrophotometer (V-670 JASCO) at room temperature in the wavelength range of 200–2000 nm. Photoluminescence (PL) spectra of the films are recorded using a 350 nm He–Cd laser and a JOBIN YVON HR-460 monochromator at room temperature in fluorescence emission scan mode. The electrical conductivity measurements were performed at room temperature by four-probe method. The film thickness was measured by means of a stylus profilometer.

3. Results and discussions

3.1. Structural analysis

The XRD diffraction patterns of the $MnIn_2S_4$ thin films which were deposited at various substrate temperatures (250–350 °C) are presented in Fig. 1. From the diffraction patterns, strong diffraction peaks at 2θ=14.28°, 23.45° and 27.57° assigned to (111), (220) and (311) reflection planes respectively, indicates the presence of polycrystalline cubic spinel structure [20]. This is in good agreement with JCPDS data (JCPDS file No. 4-626) and earlier reported literature [21–24]. Moreover, a few additional diffraction peaks were observed which may be formed due to the formation of intermediate complex compounds such as MnS_2, InS and In_2S_3, as a result of thermal decomposition of metal chlorides and thiocarbonamide [25–27]. It is also observed that the intensity of

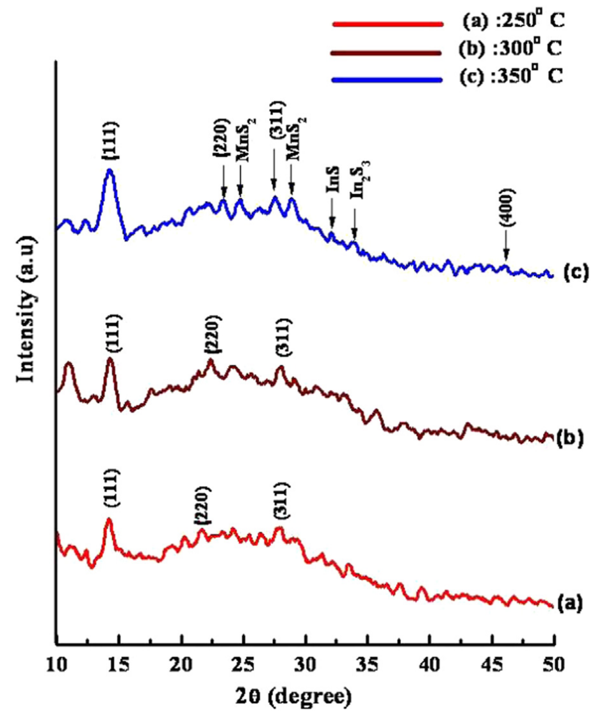

Fig. 1. X-ray diffraction spectra of $MnIn_2S_4$ thin films prepared at various substrate temperatures.

the peak corresponding to (111) plane increases with increase in substrate temperatures. This may be due to the well- ordered crystalline nature of the film at higher substrate temperatures [28].

From the X-ray diffraction pattern, the crystallite size of the thin films was calculated using the Debye – Scherrer formula [29].

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (4)$$

where, D is the grain size in nm, λ is the wavelength of CuKα = 1.5404 Å, β is the full-width at half-maximum (FWHM) of the peak in radian and θ is the corresponding diffraction angle (Bragg's angle). The average grain size was calculated and was found to be in the range between 215 and 348 nm corresponding to the prominent (111) peak. The variation of grain size with respect to substrate temperature is listed in Table 1. From Table 1, it is clear that, the grain size increases with increasing substrate temperature. This may be due to the improvement in the crystallinity of the film grown at higher substrate temperature. Further, at higher substrate temperatures, defect centres such as strain and dislocation density decreases, which greatly improves the crystallinity of the film [30].

3.2. Surface morphology

The surface morphology of the $MnIn_2S_4$ thin films for the different substrate temperatures was studied by FE-SEM and are

Table 1
Variation of grain size with substrate temperature (250–350 °C) of $MnIn_2S_4$ thin films corresponding to (111) diffraction plane.

Temperature (°C)	FWHM (β) in radians	Bragg's angle (2θ)	Particle size (nm)
250	1.16	14.24	215
300	1.075	14.38	227
350	0.7	14.40	348