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Properties of spray deposited nano needle structured Cu-doped Sn_2S_3 thin films towards photovoltaic applications

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ABSTRACT

Nano needle structured Cu-doped Sn_2S_3 thin films with different Cu concentrations (0, 1, 2 and 3 wt.%) were prepared by spray pyrolysis technique on glass substrates maintained at 400 °C. XRD analysis showed that the undoped and doped Sn_2S_3 films exhibit orthorhombic crystal structure with a preferential orientation along the (2 1 1) plane. SEM images confirm the presence of nano needles in both the undoped and doped films. Optical band gap is red shifted from 1.96 eV to 1.86 eV with increase in Cu concentration in the films which may be attributed to Moss-Burstein effect. All the films have resistivity in the order of 10^{-1} Ω-cm and the Sn_2S_3 film coated with 2 wt.% Cu concentration exhibit a minimum resistivity of 0.335×10^{-1} Ω cm. The obtained results infer that Sn_2S_3 film coated with 2 wt.% Cu concentration exhibit better physical properties.

1. Introduction

The binary semiconducting tin sulfide thin films such as SnS, SnS_2 and Sn_2S_3 finds applications in photovoltaic devices [1], near infrared detectors and optical recording medium [2] due to their narrow band gaps and potential abilities of multiple exciton generation upon the absorption of a single photon. Among the tin sulfide films, Sn_2S_3 is a IV–VI chalcogenide which normally crystallize in orthorhombic crystal structure with a band gap of 0.95 eV to 2.2 eV [3]. The highly anisotropic conduction exhibited by Sn_2S_3 make it a suitable semiconductor material for building photovoltaic p–n or p–i–n structures [4]. Sn_2S_3 films could be used to prepare near-lattice-mismatch hetero junctions such as Sn_2S_3/CdTe, Sn_2S_3/GaSb, Sn_2S_3/AlSb, etc., which find applications in the detection and generation of infrared radiations [2]. Sn_2S_3 films have been prepared by different techniques such as spray pyrolysis [5], plasma-enhanced chemical vapour deposition (PECVD) [6] and chemical bath deposition [7]. Among these techniques, spray pyrolysis is a promising technique for the preparation of semiconducting thin films, especially if they are used in energy conversion applications [8]. It has been reported earlier that Sn_2S_3 exhibits a high resistivity of 10^5 Ω cm at room temperature and the increased number of grains that contain this compound inevitably affected the resistivity of this film [9]. Further, it was reported that Sn_2S_3 films with tin vacancies show p-type conductivity, while the films with sulfur vacancies show n-type conductivity [10]. The main defects responsible for the conductivity of Sn_2S_3 thin films are Sn vacancies which act as acceptor defects and S vacancies which act as electron traps. In Sn_2S_3, the formation energies of the two vacancy defects are close in energy, which indicates that carrier concentrations should be sensitive to the growth or annealing conditions, and furthermore, the major carrier type might be subject to change. In photovoltaic applications, mixed type Sn_2S_3 would be detrimental to transport properties which would lower the photovoltaic device performance. So to improve the photovoltaic device performance, single phase Sn_2S_3 film is essential which can be achieved by controlling the Sn and S vacancies. It has been generally considered that the formation of p-type Sn_2S_3 is very difficult because of strong self-compensation effect due to sulfur vacancies and the depth of the acceptor level. To form a single phase Sn_2S_3 of p-type, it is essential to control the self-compensation effect of sulfur vacancies which can be achieved through doping. It has been reported earlier that Cu behaves as an acceptor type impurity which strongly influence the photo-response characteristics of CdS thin films [11]. Also it has been reported that Cu^{1+} ions when introduced in CdS lattice, quenches its photocurrent and for high Cu doping level,

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CdS films exhibit high p-type conductivity [12]. So motivated by this fact, in the present work Cu-doped Sn_2S_3 films were fabricated by spray pyrolysis technique with different Cu concentrations (0, 1, 2, and 3 wt.%) and the effect of Cu doping on the physical properties of Sn_2S_3 films was investigated and the results are reported.

2. Experimental details

Cu-doped Sn_2S_3 thin films were deposited by spray pyrolysis technique using tin (II) chloride, ($SnCl_2{\cdot}2H_2O$) (0.02 M) and thiourea $SC(NH_2)_2$ (0.02 M) as precursor salts. First $SnCl_2$ is dissolved in a mixture of HCl and deionized water in the volume ratio of 1:5 (in total 30 ml volume) while thiourea was dissolved in deionized water. HCl is used to enhance the solubility of $SnCl_2$. To achieve Cu-doping, $CuCl_2$ with different concentrations (0, 1, 2, and 3 wt.%) were added to the starting solution. The resultant solution was sprayed on glass substrates maintained at 400 °C, with the help of compressed air at a flow rate of 6 ml/min. The thickness of the films was calculated by using a stylus profilometer (SJ-301) and the thicknesses of the Sn_2S_3 films coated with Cu concentrations 0, 1, 2 and 3 wt. % were found to be equal to 245, 283, 228 and 238 nm respectively. XRD patterns of the films were obtained with the help of X-ray diffractometer (PANalytical-PW340/60 Xpert PRO) with CuKα radiation (λ = 1.5406 Å) X-ray source. The surface morphology and composition of the films were examined using scanning electron microscope (HITACHI S-3000H) and energy dispersive X-ray analysis respectively. Optical transmission spectra were obtained using a UV–vis–NIR double beam spectrophotometer (LAMBDA-35) in the wavelength range of 300–1100 nm.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the XRD patters of Sn_2S_3 films coated with different Cu concentrations (0, 1, 2 and 3 wt.%). All the films exhibited a well-defined peak at about 31.706° corresponding to the (2 1 1) plane and a weak intensity peak at 66.574° corresponding to the (4 2 2) plane of orthorhombic crystal structure (JCPDS card No. 75-2183). Besides these no extra peaks corresponding to any phase of tin sulfide were observed in these patterns confirming that the as deposited films were of Sn_2S_3 phase only. The strong (2 1 1) plane growth observed here exactly matches with the results reported by Chen et al. [10] for Sn_2S_3 films prepared on ITO glass substrates by potentiostatic electro-deposition technique. It is observed that the peak intensity of the (2 1 1) plane increased with increase in copper concentration up to 2 wt.% and above this concentration it decreases. The XRD patterns also showed that the (2 1 1) peak gets

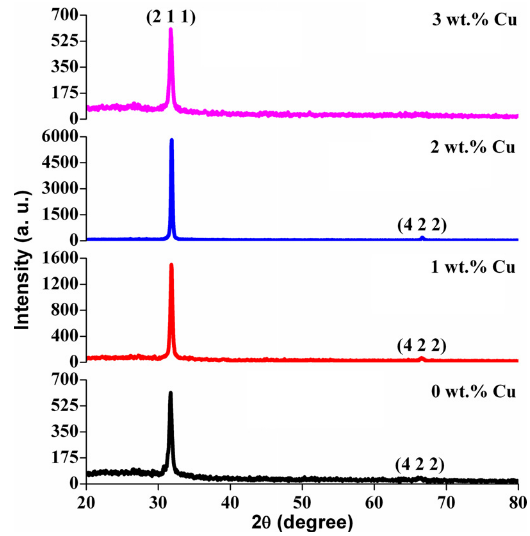

Fig. 1. XRD patterns of Cu-doped Sn_2S_3 thin films.

narrowed with increase in copper concentration up to 2 wt.% and it gets widened above this concentration. The crystallite size (D) is calculated from the Scherrer formula [13]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

where λ is the wavelength of the X-ray used (1.5406 Å), β is the full width at half maximum (FWHM) and θ is the Bragg's angle. The calculated crystallite size values are compiled in Table 1[c].

It is observed that the 2θ value of the (2 1 1) plane shift towards higher Bragg angle (Table 1) which means a contraction in the lattice volume. The lattice parameters were calculated using the following equation [14]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2)$$

and the obtained values are given in Table 1[d].

The strain (ε) in the films can be obtained using the relation [15]:

$$\varepsilon = \frac{\beta\cos\theta}{4} \quad (3)$$

and the obtained strain values are presented in Table 1[e].

3.2. SEM analysis

Fig. 2(a)–(d) shows the SEM images of Cu-doped Sn_2S_3 thin films. Nano sized shiny needle shaped grains are evinced for both the undoped and doped films. The surface of the undoped film

Table 1
Structural and optical parameters of Cu-doped Sn_2S_3 thin films.

Cu doping concentration (wt.%)	$2\theta_{(2\,1\,1)}$	$d_{(2\,1\,1)}$ Å	Crystallite size, D (nm)	Strain, $\varepsilon \times 10^{-3}$	Lattice parameters (Å)			Optical band gap, E_g (eV)	Urbach energy, E_u ($\times 10^{-4}$ eV)
					a	b	c		
0	31.706°	2.8222	27.97	1.239	5.644	15.622	5.684	1.96	0.1
1	31.836°	2.8109	33.69	1.029	5.622	15.560	5.661	1.92	0.13
2	31.864°	2.8085	41.98	0.826	5.617	15.547	5.656	1.86	0.151
3	31.743°	2.8190	34.61	1.027	5.638	15.605	5.677	1.90	0.150

[c] It is observed that the crystallite size values increases with copper concentration and the Sn_2S_3 film coated with 2 wt.% Cu concentration is found to have maximum value of crystallite size which confirms the improved crystallinity of this film.
[d] It is observed that the lattice parameter values decrease with increasing Cu concentration which may be attributed to the substitutional incorporation of Cu^+ ions into the Sn^{2+} sites. This inference is arrived, because the ionic radius of Cu^+ (0.73 Å) is slightly lesser than that of Sn^{2+} (0.93 Å). A slight decrement in the d-spacing values observed with Cu doping (Table 1) strongly favours for this supposition.
[e] It is observed that the strain value decreases with increasing Cu concentration up to 2 wt.% and above this concentration it slightly increases. The minimum value of strain observed for the Sn_2S_3 film coated with 2 wt.% Cu concentration supports for its improved crystallinity.