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Effect of substrate temperature on the physical properties of co-evaporated Sn_2S_3 thin films

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ABSTRACT

We report the deposition of tin sulfide (Sn_2S_3) thin films by co-evaporation technique at different substrate temperatures. The influence of substrate temperature on the structural and optical properties of the thin films is investigated. X- ray diffraction (XRD) analysis and Micro-Raman studies confirm the formation of Sn_2S_3 phase. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to examine the surface morphology. The transmission spectra of the deposited Sn_2S_3 thin films have been recorded in the wavelength range of 200–3000 nm using UV–vis-NIR spectrometer. Film thickness (d) and optical constants such as refractive index (n), extinction coefficient (k), real (ε_1) and imaginary (ε_2) parts of the dielectric constants of thin films are estimated from the optical transmittance. The optical band gaps of the deposited films at different substrate temperatures are in the range of 1.46–1.64 eV. Hall effect measurements confirm the n-type nature of the as-prepared Sn_2S_3 thin films.

1. Introduction

In recent years, binary and ternary semiconducting chalcogenide thin films such as CuS [1], Sn_xS_y [2], Cu_2SnS_3 [3], $AgInSe_2$ [4] have been attracting much interest due to their potential application in optoelectronic devices and solar cells. Dittrich et al. [5] have observed the importance of sulfo-salts materials in the field of optoelectronic applications. The optoelectronic properties of Sn–S based compounds are suitable for building photovoltaic p-n or p-i-n structures with high conversion efficiency of the order of 25% [6]. Tin chalcogenide thin films (SnS, SnS_2 and Sn_2S_3) belong to the family of IV-VI group semiconductor materials. These semiconductor thin films are made up of inexpensive, non-toxic and earth abundant [7] constituents. SnS and SnS_2 have been used for many applications such as absorbers [8] and window layers [9] in thin film solar cells because of their suitable optical and electrical properties. Among the tin chalcogenides, Sn_2S_3 is a semiconductor having layered structure and is a type I mixed valance compound. The optical and electrical property of Sn_2S_3 thin films depends on the crystalline structure and stoichiometry. These films are suitable for the fabrication of near lattice-matched hetero junctions like Sn_2S_3/CdTe, Sn_2S_3/GaSb, Sn_2S_3/AlS, which find applications in the detection and generation of infrared radiation [10]. Different direct band gap values such as 0.95 eV [11], 1.16 [10] and 2.0 eV [12] are reported for the of Sn_2S_3 thin films with highly anisotropic conduction nature [13]. Sn_2S_3 thin films have been prepared using different methods such as spray pyrolysis [2,10,12,14,15], potentiostatic electrodeposition [16], Plasma-Enhanced Chemical Vapor Deposition [17] and chemical bath deposition [18].

In the present work, the deposition of Sn_2S_3 thin films has been carried out by co-evaporation technique, for the first time. In this investigation Sn_2S_3 thin films are deposited on soda lime glass substrates at different substrate temperatures from 150 °C to 300 °C. The structural, morphological and electrical properties of the co-evaporated Sn_2S_3 thin films are studied and reported here. The optical properties such as refractive index n (λ), extinction coefficient k (λ) and dielectric constant (ε) of the deposited films studied and reported for the first time using the interference phenomena in transmission spectra data.

2. Experimental

Tin sulfide (Sn_2S_3) thin films have been deposited on glass substrates at different substrate temperatures from 150 °C to 300 °C at intervals of 50 °C using co-evaporation technique.

Tin wire (Sigma-Aldrich, 99.999%) and Sulfur powder (Sigma-Aldrich) were taken as source materials. Tin wire evaporated from molybdenum boat by applying a constant power and sulfur powder was evaporated from a glass crucible kept in a tungsten basket. In this technique, the source to substrate distance was fixed at 22 cm. The evaporation was carried out in a high vacuum chamber with ultimate vacuum of the order of 3.5×10^{-6} Torr. After

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reaching the evaporation temperature of source materials, shutter over the boats was moved to sideways for the deposition of the Sn_2S_3 thin film on the glass substrates [3,19]. The rate of deposition and thickness of the films was determined using SQM 160 quartz crystal thickness monitor. Prior to the deposition process, the glass slides were first cleaned with detergent solution and then thoroughly washed in running water. These slides were cleaned with Isopropyl alcohol, double distilled water and followed by ultrasonic cleaning for 30 min. These substrates are dried under infrared (IR) lamp (200 W) and cleaned with acetone. Finally, these cleaned substrates were loaded into the substrate holder of vacuum chamber. The substrates were further cleaned by ion-bombardment (HT) in vacuum chamber for ten minutes, prior to the deposition of the film. A 1KW heater with PID controller was used as the substrate heater.

X- ray diffractometer (RIGAKU ULTIMA III) with a CuK_α radiation source ($\lambda = 1.5406$ Å), was used to confirm the structure and phases of the deposited films. Raman spectroscopy was carried out to identify the phases present in the Sn_2S_3 thin films using Horiba labRAM HR evolution micro Raman spectrometer. The Scanning electron microscopy (Zeiss Ultra 55 FE-SEM) and Energy dispersive spectroscopy (EDX) were used to analyze the morphology and composition of the films deposited at different substrate temperature. The atomic force microscopy (AFM- Park NX10) was used to study the morphology of the films. The optical transmittances versus wavelength measurements were carried out using UV–vis-NIR spectrometer (JASCO V-670) in the range of wavelength 200–3000 nm. Hall measurement technique (ECOPIA HMS-5000) was employed for electrical measurements using vander pauw configuration.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the X-ray diffraction patterns of the as-deposited Sn_2S_3 thin films at different substrate temperatures on glass substrate. The diffraction peaks observed for the as-deposited samples are at 2θ values of 15.24°, 21.33°, 23.60°, 26.41°, 27.57°, 30.94° and 31.93°, which represent (120), (130), (220), (111), (140), (310) and (211) planes respectively. These values are in close agreement with the standard orthorhombic phase of the Sn_2S_3 (JCPDS 14-0169). At lower deposition temperature (150 °C) the films shows preferential orientation along (120) plane and upon increasing the deposition temperature beyond 150 °C; it is observed that the preferential orientation is along (130) plane of Sn_2S_3. It indicates that maximum number of crystallites have a growth orientation along (130) direction. Guneri et al. [18] also observed a similar (130) preferred orientation for Sn_2S_3 thin films grown by chemical deposition. From the XRD data lattice parameters are calculated using the relation

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

where d is the inter planar distance and (hkl) are the miller indices. The calculated lattice parameter values are a = 8.77 Å, b = 14.23 Å, and c = 3.77 Å. These values are closer to the orthorhombic system of Sn_2S_3 (JCPDS 14-0169). The average crystallite size (D) of the films are determined by Debye- Scherer formula [20] given by

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

where λ is the wavelength of the X-ray radiation (1.54 Å), θ is the Bragg angle and β is the full width at the half maximum (FWHM) of the (130) peak. The FWHM and average crystallite size values of as-deposited Sn_2S_3 thin films are tabulated in Table 1. These values are very closer to the crystallite values reported by Guneri et al. [18] using chemical deposition.

The instrumental broadening and physical factors such as crystallite size, micro strain and dislocation density are found to influence the width of the XRD peak of thin films. The micro stain (ε) and dislocation density (δ) are calculated using the formulae.

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

and

$$\delta = \frac{15\varepsilon}{aD} \quad (4)$$

where a is the lattice constant and D is the average crystallite size of the films. The values of micro strain (ε) and dislocation density (δ) of Sn_2S_3 thin films are tabulated in Table 1. From the table it is observed that the average crystallite size of the films increases up to 250 °C beyond that decrease with increase of substrate temperature. The decrease in the crystallite size and increase in micro strain and dislocation density of the film deposited at the substrate temperature of 300 °C can be understood from the following: at higher temperatures scattering of the atoms from heated substrate surface might restrict the formation of clusters of crystallites and might lead to low grain size [21]. Reddy et al. [7] also observed that the variation of the micro strain, dislocation density of the films decreased proportionately and correspondingly the crystallite size increased with the increase of the substrate temperature.

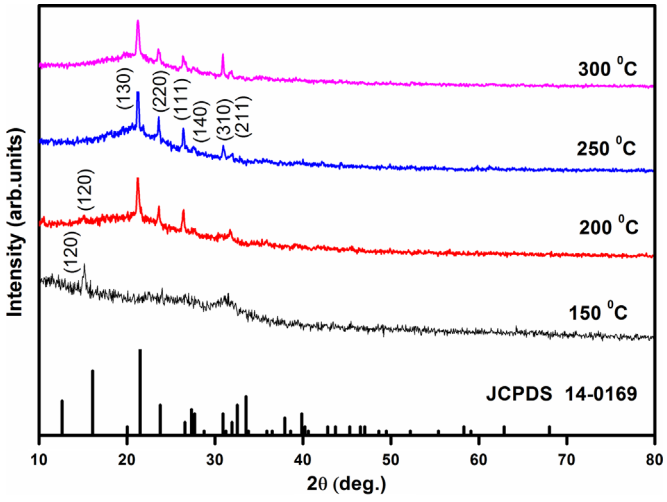

Fig. 1. X-ray diffraction patterns of Sn_2S_3 thin films at different substrate temperatures.

3.2. Raman analysis

The Raman spectra of the as-deposited Sn_2S_3 thin films in the

Table 1
Structural parameters of the Sn_2S_3 thin films at different substrate temperatures.

Substrate temperature (°C)	FWHM (β) (radians)	Crystallite size (D) (nm)	Micro strain (ε)	Dislocation density (δ) $\times 10^{16}$ (m^{-2})
150	–	–	–	–
200	0.4762	17	0.117	11
250	0.4366	20	0.107	9.46
300	0.4514	18	0.110	10.06