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Structural Morphological and Optical Properties of $SnSb_2S_4$ Thin Films Grown by Vacuum Evaporation Method

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$SnSb_2S_4$ thin films were prepared from powder by thermal evaporation under vacuum of 1.33×10^{-4} Pa (10^{-6} Torr) on unheated glass substrates. The effect of thickness on the structural, morphological and optical properties of $SnSb_2S_4$ thin films was investigated. Films thickness measured by interference fringes method varied from 50 to 700 nm. X-ray diffraction analysis revealed that all the $SnSb_2S_4$ films were polycrystalline in spite without heating the substrates and the crystallinity was improved with increasing film thickness. The microstructure parameters: crystallite size, strain and dislocation density were calculated. It was observed that the crystallite size increased and the crystal defects decreased with increasing film thickness. In addition, by increasing the film thickness, an enhancement in the surface roughness root-mean-square (RMS) increased from 2.0 to 6.6 nm. The fundamental optical parameters like band gap, absorption and extinction coefficient were calculated in the strong absorption region of transmittance and reflectance spectrum. The optical absorption measurements indicated that the band (E_g) gap of the thin films decreased from 2.10 to 1.65 eV with increasing film thickness. The refractive indexes were evaluated in transparent region in terms of envelope method, which was suggested by Swanepoul. It was observed that the refractive index increased with increasing film thickness.

KEY WORDS: Ternary system; Thermal evaporation technique; Thin films; Thickness; Atomic force microscopy (AFM)

1. Introduction

Sulfosalts or thiosalts family, created by chemistry during the XIXth century[1], belong to a class of complex sulfides minerals with the general formula $A_mB_nX_p$, where A stands for metallic elements like Cu^{1+}, Ag^{1+}, Pb^{2+}, Sn^{2+}, Fe^{2+}, Mn^{2+}, Hg^{2+}…; B represents semi-metallic elements such as As^{3+}, Sb^{3+}, Bi^{3+} and X can be either sulfur S or selenium Se[2]. Study of the phase equilibrium and crystal chemistry of the systems Sn−Sb−S sulfosalt given in literature[3] shows that these compounds are characterized by complex chemistry and complex crystal structures. Recently, sulfosalts semiconductors thin films have gained considerable interest because of their potential applications in many technological fields such as: thermoelectric energy conversion application[4], phase change memory devices[5], X-rays detectors[6], and thin film solar cells[7]. Dittrich et al.[8] studied different materials for photovoltaics and suggested "sulfosalt" to be a new absorber for solar cell applications. Several methods have been used to prepare sulfosalt layers such as: PVD[9], RF sputtering[10], spray pyrolysis[11], pulsed laser deposition[12,13], and sonochemical synthesis[14]. A great deal of interest has been focused on the growth of the promising materials of thiosalts tin antimony sulfur which may be used as an absorber material in photovoltaic solar cells. The ternary compound $SnSb_2S_4$ has a high optical absorption coefficient of almost 10^5 cm^{-1}[15] and optical band gap varying from 1 to 2.75 eV depending on the method preparation[16,17]. In addition, as part of study of the section $SnS-Sb_2S_3$, Smith and Parise[18] determined the structure of $SnSb_2S_4$ by high-resolution transmission electron microscopy (HRTEM). They have demonstrated that the $SnSb_2S_4$ structure consists of ribbons of edge-sharing semi-octahedra MX_5 (M = Sn, Sb) with space group $Pnnm$ and lattice parameters a = 2.564, b = 2.038 and c = 0.390 nm[18]. In order to exploit $SnSb_2S_4$ for large-scale electronic and optoelectronic device applications, it is essential to have a better understanding of the factors that control the

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properties of $SnSb_2S_4$ thin films. However, the effect of thickness on the properties of tin antimony sulfide thin films was seldom reported. In this paper, we investigated the structural, morphological and optical properties of the $SnSb_2S_4$ thin films grown by vacuum evaporation method.

2. Experimental

2.1. Synthesis of $SnSb_2S_4$

The initial ingot of $SnSb_2S_4$ material was grown using the horizontal Bridgman method. Stoichiometric amount of 99.99% pure Sn, Sb, and S were used. The growth of crystals was carried out in quartz ampoule, which was pre-cleaned by chemical etching in concentrated acid HF, washed in distilled water then with acetone, and finally, dried in oven at 150 °C for 30 min. The ampoule containing the pure elements were sealed under vacuum of 1.33×10^{-4} Pa (10^{-6} Torr), transferred to a programmable furnace (Nabertherm-Allemagne) and then heated slowly (10 °C/h) up to 600 °C. A complete homogenization could be obtained by keeping the melt at this temperature for about 51 h. To avoid cracking due to the thermal expansion of the melt upon solidification the ampoule was cooled at a rate of 10 °C/h. The compound obtained by this process is black and this form of ingot surface dotted with many shiny crystals of small sizes (Fig. 1), which will be crushed into fine powder to use as a filler in the evaporator for the development of thin films.

2.2. Film preparation

Thin films of $SnSb_2S_4$ were prepared by thermal evaporation from a molybdenum boat on non-heated glass substrates of rectangular shape (2.5 cm × 1.5 cm) under vacuum of 1.33×10^{-4} Pa (10^{-6} Torr) using a high vacuum coating unit Alcatel. The substrates were placed directly above the source at a distance of 15 cm. Glass substrates were previously cleaned with washing agents (commercial detergent, acetone, ethanol and deionized water) before being introduced into the vacuum system. Film thickness was measured by interference fringes method[19] and varied from 50 to 700 nm.

2.3. Characterization of powders and thin films

Crystallite phases and crystal orientations of the powders and the prepared films were analyzed using a Philips PW 3710 with Cu$K\alpha_1$ radiation ($\lambda = 0.15406$ nm). The surface morphology of the films was probed with the atomic force microscopy (Veeco D 3100 AFM). The optical transmittance and reflectance were recorded at normal incidence in the wavelength range of 300−1800 nm using a Shimadzu UV-visible-NIR spectrophotometer.

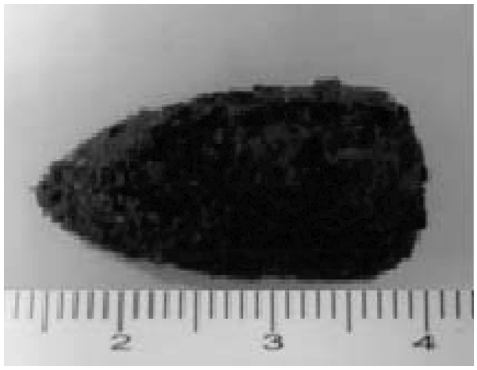

Fig. 1 Ingot of $SnSb_2S_4$ crystal.

3. Results and Discussion

3.1. Structural study

X-ray diffraction (XRD) patterns were used to study the structural properties of $SnSb_2S_4$ powder. Fig. 2 shows the typical XRD pattern of the $SnSb_2S_4$ powder. This figure indicates that the material is polycrystalline with (621) preferred orientation. The diffraction peaks in the XRD pattern could be indexed to pure orthorhombic crystal structure of $SnSb_2S_4$ with space group of *Pnnm* and no diffraction peaks corresponding to impurities like Sb_2O_3 and SnO_2 were observed, which confirms that the as-synthesized product was single phase of pure $SnSb_2S_4$. Given the Bragg relation $2d \sin\theta = \lambda$ and the inter-planar spacing for an orthorhombic system, the lattice constants a, b and c of the $SnSb_2S_4$ compound were determined and the values are 2.549, 2.048 and 0.383 nm, respectively. These values are in good agreement with standard (JCPDS) database with card number 35-1496[18].

Fig. 3 displays XRD patterns of $SnSb_2S_4$ films grown at room temperature with different thickness in the range of 50−700 nm. It is clear from Fig. 3 that $SnSb_2S_4$ layer prepared with thickness of 50 nm is amorphous in nature while those prepared with thickness above or equal to 150 nm are polycrystalline in nature with a preferred orientation along the $SnSb_2S_4$ (621) plane with orthorhombic structure, as found by several authors[20]. The overall feature of this compound $SnSb_2S_4$ is that all the deposited films are crystallized, in spite without heating the substrates. Furthermore, with increasing film thickness, the crystalline quality of $SnSb_2S_4$ layers is enhanced. Also, the (621) peak intensity increases gradually with increasing film thickness. This shows an improvement in crystallinity with increasing film

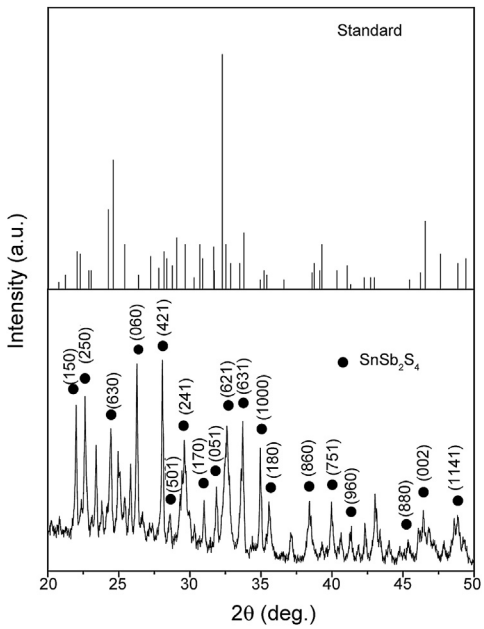

Fig. 2 XRD patterns of standard and as-synthesized $SnSb_2S_4$ powder.