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Thermal annealing of SnS thin film induced mixed tin sulfide oxides-Sn_2S_3 for gas sensing: Optical and electrical properties

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ABSTRACT

This work reports the air-annealing effect on the structure, optical and electrical properties of tin sulfides (SnS) thin films and the capability of using these films for gas sensing application. The X-ray diffraction investigation shows that the predominant phase SnS (040) plane for the as-deposited film changes into Sn_2S_3 (201) plane after annealing. Furthermore, the annealed films at high temperatures (533 and 553 K) are partially oxidized leading to the formation of mixed tin sulfide oxides-Sn_2S_3 (MTO-Sn_2S_3) heterostructure thin film. The optical constants and thickness of films are calculated using Swanpole's method. Both optical band gap and electrical activation energy increased after annealing in the range (493–553 K) for 0.5 h in ambient air. Optical and electrical results indicate the existence of mixed phase characteristics of studied films. The gas sensing properties of MTO-Sn_2S_3 composite are investigated for methane gas detection. The fabricated sensor exhibits a weak sensitivity at low operating temperatures (50 and 100 °C). The sensitivity improves at high temperatures reaching its maximum at 250 °C. At 250 °C the response and recovery times are 250 and 82 s, respectively.

1. Introduction

Among tin sulfide family, SnS (1:1) film is a *p*-type semiconductor due to the low formation energy of Sn vacancies which create acceptor levels [1]. It has optical gap ranging from 1.1 to 1.7 eV depending on the preparation conditions, crystal structure [2–4] and the existence of other phases SnS_2 or Sn_2S_3 [5]. In recent years, SnS contributed intensively to green technology applications because it is cheap and non-toxic [6]. Its tunable band gap makes it suitable for photovoltaic applications; also SnS has been used in gas sensors, holographic recording media and photodetectors [7–9]. Another interesting member of this family is the Sn_2S_3 compound, its *n*-type semiconductor with wide-ranging band gap (0.95–2.2 eV) [10–15].

Gas sensing devices are essential in many aspects of technology, industry, or daily life. Fast and reliable detection of hazardous gases in low concentration is vital in fields such as industrial plants, nursing, environmental monitoring, or air quality assurance. So, development of gas sensing materials is essential to overcome diverse challenges in terms of sensitivity, selectivity of response, robustness, and many other aspects. Thin film semiconductor-based gas sensors include five types, resistor, diode, metal-insulator-semiconductor (MIS) capacitor, metal-insulator-semiconductor field effect transistor (MIS FET) and oxygen concentration cell [16]. Resistive sensors are favorable over other types as it is easy to fabricate and is capable to direct measurement [17]. Tin sulfide composites have been used for gas sensor fabrication. Namely, SnS-SnO_2 composites have been used to investigate oxygen sensing properties. [18,19] measured the response of SnS sensor to inflammable (reducing) gases such as alcohols and acetone. Developed a novel gas sensor based on 2D SnS_2 was flaked with a very strong selectivity to NO_2 molecules at low operating temperatures less than 160 °C [20]. Also, it was found that SnS_2 nanorods sensor has strong selectivity versus carbonyl group of aldehydes and ketones [21]. Recently, oxidizing gas sensing properties of based Sn_2S_3 semiconductor sensor was researched [22].

This work aims to prepare mixed tin sulfide oxides-Sn_2S_3 by the thermal annealing of the as-deposited SnS film. Structures, optical and electrical properties of the as-deposited and thermal annealed SnS films are studied. The Sn_2S_3 based sensor fabrication and gas response measurements are achieved.

2. Experimental techniques

2.1. Thin film preparation and characterization

High-purity (99.99%) tin and sulfur powders were mixed in an atomic ration of S: Sn = 1:1 with a total mass of 0.5 g are sealed into

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silica ampoule under vacuum of 10^{-5} Torr. The ampoule was kept in a furnace at 450 °C for 24 h and 700 °C for 48 h to ensure complete homogenization. Finally, the melt was lowered to room temperature. Tin sulfide films were thermally evaporated from SnS ingots using a high vacuum coating unit (Edwards E-306) on glass microscopic slides, with dimensions of 1.6 × 2.3 cm^2. Structure nature of thin films was synthesized using Philips X-ray diffractometer with a monochromatic CuKα radiation (λ = 1.54056 A°). Energy dispersive X-ray analysis (EDX) was employed to specify the elemental composition present in the as deposited film. A double-beam spectrophotometer (Shimadzu UV-2101) was used to record transmittance (T) and reflectance (R) at room temperature. Photoluminescence (PL) measurements (Jasko, FP-6300 WRE) in range (300–900 nm) were recorded to analyze the emission at two excitation wavelengths λ_{ex} = 380 nm and λ_{ex} = 558 nm. Dark electrical measurements were done using keithly (610 C Electrometer) in temperature range (300–503 K).

2.2. Sensor fabrication and gas sensing measurements

The fabrication of mixed tin sulfide oxides-Sn_2S_3 (Hereafter it will be referred to as MTO-Sn_2S_3) composite gas sensor consisted of two stages. First, the as evaporated SnS film was annealed at 280 °C for 0.5 h in ambient air. This process resulted in a formation of Sn_2S_3 phase with partial oxidation of the film surface, yielding the constructing of MTO-Sn_2S_3 hetrostructure thin film. Second, two Aluminum electrodes with thickness of 100 nm were thermally deposited on the film surface to collect the gas sensor electrical response. The deposited electrodes dimensions were 1.6 × 1.05 cm^2 for each with separation of 0.2 cm.

2.3. Gas sensing measurements

The fabricated sensor response was measured at diverse operating temperatures for methane sensing. The sensor was placed in a cylinder quarts tube, which was inserted into an electric furnace. The electrical signal through Al electrodes was collected using computerized data acquisition instrument (LXI Agilent 34972 A) at constant voltage of 5 V. The reducing gas (CH_4) was injected into the chamber at a flow rate of 200 ml/min. Both methane and air passed over the sensor sequentially using Horiba mass flow controllers (SEC-N112 MGM).

3. Results and discussion

3.1. Structural analysis

Energy dispersive X-ray analysis (EDX) for as-deposited SnS thin film indicated that the atomic percentage rations of Sn and S are around 47.9 and 52.1, respectively. Fig. 1 shows XRD patterns of SnS thin films of thickness 475 nm, as-deposited and thermal annealed films at different temperatures. In this figure, the presence of several diffracted peaks confirms the crystalline structure of as deposited and thermal annealed films. The crystalline phases and their orientation along different directions are identified from International Centre for Diffraction Data (ICCD) files as presented in Fig. 1. The XRD spectra of the as-synthesized SnS film shows dominant orthorhombic SnS phase at 2θ = 31.38° with (040) preferred orientation. Reddy et al. [23] have observed a similar (040) main diffraction for SnS thin films using co-evaporation technique for film deposition. Fig. 1a reveals other less intense peaks at 2θ = 30.4°, 38.86°, 44.44°, 50.98°, which are also assigned to the orthorhombic SnS phase and 45.22° assignable to Sn_2S_3 phase. On the other hand, the main diffraction peak for annealed films can be assigned to the orthorhombic Sn_2S_3 phase (card num. 00-014-0619).

For high temperature annealed films at 533 and 553 K, (Fig. 1c and d), it is observed the presence of other phases besides the main Sn_2S_3 phase. Namely, for annealed film at 533 K, (Fig. 1c) the noticed peaks at 2θ = 28.06°, 52.12° can be assigned to the $Sn(SO_4)$ and SnO orthorhombic phases, respectively. This refers to the partial oxidation of high temperature annealed films. Yuea [24] has reported fully oxidation for SnS films upon annealing at 523 K in air. At the annealing temperature (T_a) = 553 K (Fig. 1d), the diffracted peaks at 2θ = 28.06°, 31.24°, 38.8°, 44.32°, 49.66°, 52.12° can be indexed to the Sn (SO_4), Sn_2S_3, Sn_2S_3, SnO, Sn_2S_3 and SnO phases, respectively. This asserts the formation of MTO-Sn_2S_3 hetrostructure thin film.

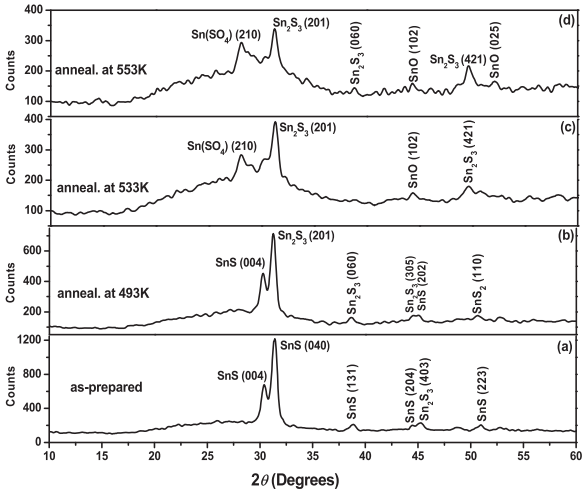

Fig. 1. XRD patterns for as-prepared annealed SnS thin films of thickness 475 nm.

For further analyses, Fig. 2 shows a representative example of the induced structure changes by thermal treatment of prepared films. As we can see, the main diffraction peak shifted to lower angle, which may resulted from expanding the volume unit cell after air annealing. A large decrease in intensity of the main peak as T_a increases is observed.

The size of crystallite for different films was estimated for the main peak of each film, using Scherer's formula:

$$D = \frac{0.9\,\lambda}{B\,\cos\theta}. \quad (1)$$

Residual strain (ε) of tin sulfide films is estimated from [25]:

$$\varepsilon = \left[\frac{\lambda}{D\cos\theta} - B\right]\frac{1}{\tan\theta}. \quad (2)$$

The density dislocations (δ), defined as the length of dislocation lines per unit volume, is evaluated from [26]:

$$\delta = \frac{1}{D^2}. \quad (3)$$

Where D, λ, B, and θ are the crystallite size, X-ray wavelength, the full width at half maximum height and Bragg angle, respectively. From Table 1, the estimated crystallite size decreases from 16 nm to 13 nm

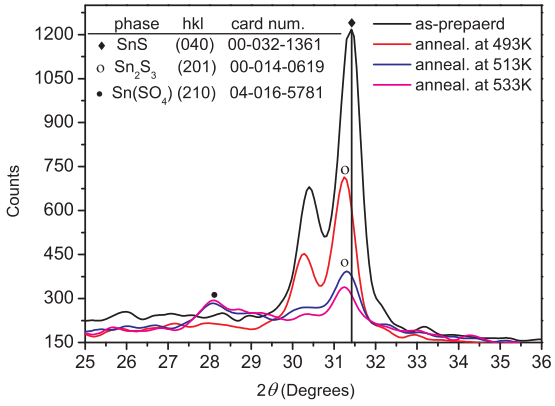

Fig. 2. XRD pattern of the main peak for as-prepared annealed SnS thin films.